THE DL_POLY_2 USER MANUAL

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ABOUT DL_POLY

DL_POLY is a parallel molecular dynamics simulation package developed at Daresbury Laboratory by W. Smith and T.R. Forester under the auspices of the former Engineering and Physical Sciences Research Council (EPSRC) for the EPSRC's Collaborative Computational Project for the Computer Simulation of Condensed Phases (CCP5) and the Advanced Research Computing Group (ARCG) at Daresbury Laboratory. The package is the property of The Council for the Central Laboratory of the Research Councils (CCLRC).

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The purpose of the DL_POLY package is to provide software for academic research that is inexpensive, accessible and free of commercial considerations. Users have direct access to source code for modification and inspection. In the spirit of the enterprise, contributions in the form of working code are welcome, provided the code is compatible with DL_POLY in regard to its interfaces and programming style and it is adequately documented.

DISCLAIMER

Neither the CCLRC, EPSRC, CCP5 nor any of the authors of the DL_POLY_2 package or its derivatives guarantee that the package is free from error. Neither do they accept responsibility for any loss or damage that results from its use. Use of the DL_POLY_2 package without charge is confined to academic research only. Commercial use is only permissible following negotiation with Daresbury Laboratory. Users are not entitled to redistribute the program to third parties.

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Manual Notation

In the DL_POLY Manual and Reference Manual specific fonts are used to convey specific meanings:

1. *directories* - indicates unix file directories
2. ROUTINES - indicates subroutines, functions and programs.
3. *macros* - indicates a macro (file of unix commands)
4. **directive** - indicates directives or keywords
5. `variables` - indicates named variables and parameters
6. FILE - indicates filenames.

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Chapter 1

Introduction

Scope of Chapter

This chapter describes the concept, design and directory structure of DL_POLY_2 and how to obtain a copy of the source code.

1.1 The DL_POLY Package

DL_POLY_2 (DL_POLY [1]) is a package of subroutines, programs and data files, designed to facilitate molecular dynamics simulations of macromolecules, polymers, ionic systems and solutions on a distributed memory parallel computer. The first version was written on behalf of CCP5 [2] in the eighteen months preceding September 1993 when the (beta) release appeared. The principal authors at that stage were Bill Smith and Tim Forester at Daresbury Laboratory. For want of a more imaginative acronym the package was named DL_POLY. The entire DL_POLY project was given a major boost by the provision of a grant in January 1993 from the SERC's Computational Science Initiative. An additional grant was made by the EPSRC in June 1994 to continue developments in the period 1995-97. In April 1995 the project came under the Council for the Central Laboratory of the Research Councils.

There were many reasons for writing the package. The first reason being to exploit parallel computing for molecular simulation in the UK. There were several worthy packages available to the academic community including GROMOS [3], AMBER [4] and X-PLOR [5], but none of these were designed (as far as we were able to tell) with parallel computers in mind, (though parallel versions of these programs now exist). We decided then that the effort involved in devising a new code which had parallelism built into it from the start would be well spent. This we thought would allow us to adapt the code to new architectures with greater ease. The second reason was to bring to fruition the high level of parallel programming expertise at Daresbury Laboratory, and generally within the CCP5 community, stretching back several years, in the area of molecular dynamics. We therefore thought it worthwhile to tap into this expertise to produce a new package. The third reason was that we thought it would be valuable to produce a package that was entirely free from commercial constraints, by which we mean the source code would be available to academic institutions for adaptation and extension. There would be no restriction preventing users from examining (and verifying!) the source code. DL_POLY was not to be a "black box".

Of course, in a rapidly developing subject area, we cannot guarantee we have everything a potential user may need. However since this is very much a project endorsed by CCP5, which serves the UK (and World-Wide) academic community, we are also hopeful that our users will be inclined to contribute any extensions of the package they devise and so accelerate its development. As it stands, the package has some nice features we believe. While it is designed for distributed memory parallel machines, we have taken care to ensure that it can, with minimum modification, be run on the popular workstations. Scaling up a simulation from a small workstation to a massively parallel machine remains straightforward. This ought to encourage novices to take up parallel computing!

Users are reminded that we are interested in hearing what other features could be usefully incorporated. We obviously have ideas of our own and CCP5 strongly influences developments, but other input would be welcome nevertheless. We also request that our users respect the integrity of DL_POLY_2 source and not pass it on to third parties. We require that all users of the package register with us, not least because we need to keep everyone abreast of new developments and discovered bugs. We have developed various forms of licence, which we hope will ward off litigation (from both sides), without denying

access to genuine scientific users.

In the next section we outline the capabilities of DL_POLY_2 as briefly as possible. This is followed by a description of the DL_POLY_2 directory structure and how to obtain the source code from Daresbury Laboratory. Much more information is to be found later in this manual. Access to all this information and more can be gained via out WWW page: http://www.dl.ac.uk/TCSC/Software/DL_POLY/main.html

1.2 Functionality

The following is a list of the features DL_POLY_2 . It is worth reminding users that DL_POLY_2 represents a *package* rather than a single program, so users should consider piecing together their own program with the desired functionality. We will however, supply a consolidated program in the distributed source.

1.2.1 Molecular Systems

DL_POLY_2 will simulate the following molecular species:

1. Simple atomic systems and mixtures e.g. Ne, Ar, Kr, etc.
2. Simple unpolarisable point ions e.g. NaCl, KCl, etc.
3. Polarisable point ions and molecules e.g. MgO, H_2O etc.D
4. Simple rigid molecules e.g. CCl_4, SF_6, Benzene, etc.
5. Rigid molecular ions with point charges e.g. KNO_3, $(NH_4)_2SO_4$, etc.
6. Polymers with rigid bonds e.g. C_nH_{2n+2}
7. Polymers with rigid bonds and point charges e.g. proteins
8. Macromolecules and biological systems
9. Molecules with flexible bonds
10. Silicate glasses and zeolites
11. Simple metals e.g. Al, Ni, Cu etc.

1.2.2 Force Field

The DL_POLY_2 force field includes the following features:

1. All common forms of non-bonded atom-atom potential;
2. Atom-atom (site-site) Coulombic potentials;
3. Valence angle potentials;

4. Dihedral angle potentials;
5. Inversion potentials;
6. Improper dihedral angle potentials;
7. 3-body valence angle and hydrogen bond potentials;
8. 4-body inversion potentials;
9. Sutton-Chen density dependent potentials (for metals) [6].

The parameters describing these potentials may be obtained, for example, from the GROMOS [3], DREIDING [7] or AMBER [4] forcefield, which share functional forms. It is relatively easy to adapt DL_POLY_2 to user specific force fields.

1.2.3 Boundary Conditions

DL_POLY_2 will accommodate the following boundary conditions;

1. None e.g. isolated polymer in space.
2. Cubic periodic boundaries.
3. Orthorhombic periodic boundaries.
4. Parallelepiped periodic boundaries.
5. Truncated octahedral periodic boundaries.
6. Rhombic dodecahedral periodic boundaries.
7. Slab (x,y periodic, z nonperiodic).
8. Hexagonal prism periodic boundaries.

These are describe in detail in Appendix B.

1.2.4 Algorithms

1.2.4.1 Parallel Algorithms

DL_POLY_2 exclusively employs the **Replicated Data** parallelisation strategy [8, 9].

1.2.4.2 Molecular Dynamics Algorithms

The DL_POLY_2 MD algorithms are all couched in the form of the Verlet Leapfrog integration algorithm [10]. NVE, NVT, NPT and N$\underline{\underline{\sigma}}$T ensembles are available, with a selection of thermostats and barostats. A parallel version of the SHAKE algorithm [11] called RD-SHAKE is used for bond constraints [9]. Fincham's implicit quaternion algorithm (FIQA) [12] is available for rigid molecular species. Rigid molecular species linked by rigid bonds are handled with an algorithm of our own devising, called the QSHAKE algorithm [13].

The following MD algorithms are available:

1. Verlet leapfrog;
2. Verlet leapfrog with RD-SHAKE;
3. Rigid molecules with FIQA and RD-SHAKE;
4. Linked rigid molecules with QSHAKE [13];
5. Berendsen constant T algorithm with Verlet or RD-SHAKE [14];
6. Evans constant T algorithm with Verlet or RD-SHAKE [15];
7. Hoover constant T algorithm with Verlet or RD-SHAKE [16];
8. Berendsen constant T algorithm with FIQA and RD-SHAKE [14];
9. Berendsen constant T algorithm with QSHAKE [14];
10. Hoover constant T algorithm with FIQA and RD-SHAKE [16];
11. Hoover constant T algorithm with QSHAKE [16];
12. Berendsen constant T,P algorithm with RD-SHAKE [14];
13. Berendsen constant T,$\underline{\underline{\sigma}}$ algorithm with RD-SHAKE [14];
14. Hoover constant T,P algorithm with RD-SHAKE [16];
15. Hoover constant T,$\underline{\underline{\sigma}}$ algorithm with RD-SHAKE [16];
16. Berendsen constant T,P algorithm with FIQA and RD-SHAKE [14];
17. Berendsen constant T,P algorithm with QSHAKE [14];
18. Berendsen constant T,$\underline{\underline{\sigma}}$ algorithm with FIQA and RD-SHAKE [14];
19. Berendsen constant T,$\underline{\underline{\sigma}}$ algorithm with QSHAKE [14];
20. Hoover constant T,P algorithm with FIQA and RD-SHAKE [16];
21. Hoover constant T,P algorithm with QSHAKE [16];

22. Hoover constant T,$\underline{\underline{\sigma}}$ algorithm with FIQA and RD-SHAKE [16];

23. Hoover constant T,$\underline{\underline{\sigma}}$ algorithm with QSHAKE [16];

A variant of DL_POLY_2 that handles the time reversible, multiple timestep RESPA algorithm [17, 18] is also available for atomic systems and rigid ion systems [19], but it is not applicable to systems which have rigid body molecules or constraints.

1.3 Programming Style

The programming style of DL_POLY_2 is intended to be as uniform as possible. The following stylistic rules apply throughout. Potential contributors of code are requested to note the stylistic convention.

1.3.1 Programming Language

Versions of DL_POLY_2 prior to 2.11 are written exclusively in FORTRAN 77. Versions of DL_POLY_2 from 2.11 contain extensions written in FORTRAN 90.

1.3.2 Memory Management

Since version 2.11 of DL_POLY_2 , the major array dimensions are calculated at the time of execution and the associated arrays created through the dynamic array allocation features of FORTRAN 90. In versions prior to 2.11, array dimensions are fixed at compilation time and defined by FORTRAN PARAMETER statements

1.3.3 Target Computers

DL_POLY_2 is targeted towards distributed memory parallel computers. However, versions of the program for serial computers are easily produced. To facilitate this all machine specific calls are located in dedicated FORTRAN routines, to permit substitution by appropriate alternatives, or even deletion.

DL_POLY_2 will run on the the following computers:

1. Cray T3D
2. Cray T3E
3. DEC Alpha
4. HP 9000 Series
5. Hitachi SR2201
6. IBM RS6000
7. IBM SP/2

8. Intel iPSC/860
9. SUN SPARC and ULTRA SPARC.
10. Silicon Graphics machines (all kinds).

Porting of DL_POLY_2 to these and other machines requires PVM or MPI message passing tools, with the exception of Intel distributed memory machines.

1.3.4 Version Control System (CVS)

DL_POLY_2 was developed with the aid of the CVS version control system. We strongly recommend that users of DL_POLY_2 adopt this system for code development, particularly where several users access the same source code. For information on CVS please contact:

$$info - cvs - request@prep.ai.mit.edu$$

1.3.5 Required Program Libraries

DL_POLY_2 is, for the most part, self contained and does not require access to many additional program libraries. The required program libraries for parallel execution are either PVM or MPI (we recommend the latter). The other exception is the need for 3D Fast Fourier Transform (FFT) routines in the Smooth Particle Mesh Ewald (SPME) method introduced in Version 2.12. For applications on Cray T3E/D and IBM SP/2 computers the required routines are readily available in the scientific subroutine libraries (routines ccfft3d and dcft3 respectively). For other machines however, we have assumed the public domain FFT routine fftwnd_fft is available. The standard Ewald sum remains available for users without access to a suitable substitute.

1.3.6 Internal Data Transfer

As a general policy, there should be **NO** COMMON blocks in DL_POLY_2 . All nonlocal and large local arrays are passed as subroutine arguments. It follows that there should be no BLOCK DATA.

However the introduction of the FORTRAN 90 dynamic array allocation features in DL_POLY_2 version 2.11 has required the creation of a named COMMON block (/params/) to facilitate the passing of the array dimensions between subroutines. (Formerly the dimensions had been defined as FORTRAN parameters and incorporated in each subroutine through the include file DL_PARAMS.INC.) The COMMON block /params/ is defined in the new version of the include file DL_PARAMS.INC and is included in almost all subroutines.

Additional COMMON blocks are also required to facilitate inter-node communication via MPI and PVM.

1.3.7 Internal Documentation

All subroutines are supplied with a header block of FORTRAN COMMENT records giving:

1. The name of the author and/or modifying author
2. The version number or date of production
3. A brief description of the function of the subroutine
4. A copyright statement
5. A CVS revision number and associated data.

Elsewhere FORTRAN COMMENT cards are used liberally.

1.3.8 Subroutine/Function Calling Sequences

The variables in the subroutine arguments are specified in the order:

1. logical and logical arrays
2. character and character arrays
3. integer
4. real and complex
5. integer arrays
6. real and complex arrays

This is admittedly arbitrary, but it really does help with error detection.

1.3.9 FORTRAN Parameters

All parameters defined by the FORTRAN parameter statements are specified in the include file: DL_PARAMS.INC, which is included at compilation time in all subroutines requiring the parameters. All parameters specified in DL_PARAMS.INC are described by one or more comment cards.

Note that since the implementation of FORTRAN 90 memory management in Version 2.11, the DL_PARAMS.INC file also contains the COMMON block /params/, described above.

1.3.10 Arithmetic Precision

All real variables and parameters are specified in 64-bit precision (i.e real*8).

1.3.11 Units

Internally all DL_POLY_2 subroutines and functions assume the use of the following defined *molecular units*:

1. The unit of time (t_o) is 1×10^{-12} seconds (i.e. picoseconds).
2. The unit of length (ℓ_o) is 1×10^{-10} metres (i.e. Ångstroms).
3. The unit of mass (m_o) is $1.6605402 \times 10^{-27}$ kilograms (i.e. atomic mass units).
4. The unit of charge (q_o) is $1.60217733 \times 10^{-19}$ coulombs (i.e. unit of proton charge).
5. The unit of energy ($E_o = m_o(\ell_o/t_o)^2$) is $1.6605402 \times 10^{-23}$ Joules (10 J mol^{-1}).
6. The unit of pressure ($\mathcal{P}_o = E_o\ell_o^{-3}$) is 1.6605402×10^{7} Pascal (166.05402 bar).
7. Planck's constant ($\hbar$) which is $6.350780668 \times E_o t_o$.

In addition the following conversion factors are used:
The coulombic conversion factor (γ_o) is:

$$\gamma_o = \frac{1}{E_o}\left[\frac{q_o^2}{4\pi\epsilon_o\ell_o}\right] = 138935.4835$$

such that:

$$U_{MKS} = E_o\gamma_o U_{Internal}$$

Where U represents the configuration energy.
The Boltzmann factor (k_B) is 0.831451115 E_oK^{-1}, such that:

$$T = E_{kin}/k_B$$

represents the conversion from kinetic energy (in internal units) to temperature (in Kelvin).

Note: In the DL_POLY_2 OUTPUT file, the print out of pressure is in units of kbars at all times. The unit of energy is either DL_POLY_2 units specified above, or in other units specified by the user at run time. The default is DL_POLY units.

1.3.12 Error Messages

All errors detected by DL_POLY_2 during run time initiate a call to the subroutine ERROR, which prints an error message in the standard output file and terminates the program. All terminations of the program are global (i.e. every node of the parallel computer will be informed of the termination condition and stop executing.)

In addition to terminal error messages, DL_POLY_2 will sometimes print warning messages. These indicate that the code has detected something that is unusual or inconsistent. The detection is non-fatal, but the user should make sure that the warning does represent a harmless condition.

1.4 The DL_POLY_2 Directory Structure

The entire DL_POLY_2 package is stored in a Unix directory structure. The topmost directory is named *dl_poly_nn*, where *nn* is a generation number. Beneath this directory are several sub-directories named: *source; utility; data; bench; execute; build, public, respa, and sdk*. Briefly, the content of each sub-directory is as follows:

sub-directory	contents
source	primary subroutines for the DL_POLY_2 package
utility	subroutines, programs and example data for all utilities
data	example input and output files for DL_POLY_2
bench	large test cases suitable for benchmarking
execute	the DL_POLY_2 run-time directory
build	makefiles to assemble and compile DL_POLY_2 programs
public	directory of routines donated by DL_POLY_2 users
sdk	directory of routines used to construct the DL_POLY_2 GUI
respa	directory of routines used to construct the DL_POLY_2 RESPA program

A more detailed description of each sub-directory follows.

1.4.1 The *source* Sub-directory

In this sub-directory all the essential source code for DL_POLY_2 , excluding the utility software. In keeping with the 'package' concept of DL_POLY_2 , it does not contain any complete programs; these are assembled at compile time using an appropriate makefile. The subroutines in this sub-directory are documented in chapter 7.

1.4.2 The *utility* Sub-directory

This sub-directory stores all the utility subroutines, functions and programs in DL_POLY_2 , together with examples of data. The various routines in this sub-directory are documented in chapter 6 of this manual. Users who devise their own utilities are advised to store them in the *utility* sub-directory.

1.4.3 The *data* Sub-directory

This sub-directory contains examples of input and output files for testing the released version of DL_POLY_2 . The examples of input data are copied into the *execute* sub-directory when a program is being tested. The test cases are documented in chapter 5.

1.4.4 The *bench* Sub-directory

This directory contains examples of input and output data for DL_POLY_2 that are suitable for benchmarking DL_POLY_2 on large scale computers. These are described in chapter 5.

1.4.5 The *execute* Sub-directory

In the supplied version of DL_POLY_2 , this sub-directory contains only a few macros for copying and storing data from and to the *data* sub-directory and for submitting programs for execution. (These are decribed in section 6.1.2.) However when a DL_POLY_2 program is assembled using its makefile, it will be placed in this sub-directory and will subsequently be executed from here. The output from the job will also appear here, so users will find it convenient to use this sub-directory if they wish to use DL_POLY_2 as intended. (The experienced user is not absolutely required to use DL_POLY_2 this way however.)

1.4.6 The *build* Sub-directory

This sub-directory contains the standard makefiles for the creation (i.e. compilation and linking) of the DL_POLY_2 simulation programs. The makefiles supplied select the appropriate subroutines from the *source* sub-directory and deposit the executable program in the *execute* directory. The user is advised to copy the appropriate makefile into the *source* directory, in case any modifications are required. The copy in the *build* sub-directory will then serve as a backup.

1.4.7 The *public* Sub-directory

This sub-directory contains assorted routines donated by DL_POLY users. Potential users should note that these routines are **unsupported** and come **without any guarantee or liability whatsoever**. They should be regarded as potentially useful resources to be hacked into shape as needed by the user. This directory is available from the CCP5 Program Library by direct FTP(see below).

1.4.8 The *respa* Sub-directory

This sub-directory first appeared in Version 2.12, when the RESPA subroutines were separated from the *source* directory to make construction of the RESPA program simpler. The *respa* sub-directory consists of the subroutines unique to the RESPA application. The RESPA makefile (Makefile_respa in the *build sub-directory* has been designed to gather the additional subroutines required from the *source* sub-directory at compile time. It is not necessary for the user to copy them over.

1.4.9 The *sdk* Sub-directory

The DL_POLY_2 Graphical User Interface (GUI) is based on the CERIUS^2 Visualiser from Molecular Simulations Inc. The subroutines *written by Daresbury Laboratory* are to be found in this sub-directory. However, alone they are insufficient to create a working GUI, but DL_POLY_2 users who have access to MSI's SDK (Software Development Kit) will be able to use these subroutines as a starting place for constructing, and modifying, the DL_POLY_2 GUI. For DL_POLY_2 users without this resource, a compiled version of the GUI is available for Silicon Graphics computers running the CERIUS^2 Visualiser (version 3.5). See the document "The DL_POLY_2 Graphical User Interface", by W. Smith [20].

1.5 Obtaining the Source Code

To obtain a copy of DL_POLY_2 it is first necessary to obtain a licence from Daresbury Laboratory. A copy of the licence form may be obtained in two ways: either by selecting the licence button on the World Wide Web page:
(http://www.dl.ac.uk/TCSC/Software/DL_POLY/main.html)
and downloading and printing the file; or by using FTP to copy the postscript file from the CCP5 Program Library at Daresbury Laboratory in the following manner:

1. move to the desired directory on YOUR machine,
2. type: **ftp ftp.dl.ac.uk**
3. enter userid: **anonymous**
4. enter passwd: (use your name and site)
5. change to the CCP5 directory: **cd ccp5**
6. change to the DL_POLY directory: **cd DL_POLY**
7. type: **binary**
8. type: **get LICENCE.ps.Z**
9. type: **quit**

The licence file will need to be uncompressed (using the unix *uncompress* command) before printing. Note that there are two versions of the licence available; one for single academic users (with perhaps one or two postgraduate students); and one for academic groups (with perhaps several research staff, including postdoctoral and permanent staff.) Choose the one most suitable for you.

Once you have obtained the licence form you should sign it and return it to the following address.

```
Dr. W. Smith
DL_POLY Program Library
Computational Science and Engineering Department
CCLRC Daresbury Laboratory
Daresbury
Warrington WA4 4AD
England
```

Please return the licence**by post please**; FAXes are not acceptable to our Contracts Department. When the signed licence has been received DL_POLY_2 source code will be sent by ftp. We will need to contact you about this procedure, so **please supply your e-mail address**. Please note we cannot create accounts on any of our machines for this purpose.

The DL_POLY_2 User Manual is freely available via World Wide Web or ftp, in the same manner as the licence form. The much larger DL_POLY_2 Reference Manual will be available by the above ftp procedure only.

Daresbury Laboratory is the sole centre for the distribution of DL_POLY_2 and copies obtained from elsewhere will be regarded as illegal and will not be supported.

1.6 DLPROTEIN

DLPROTEIN is a further development of DL_POLY that was written by S. Melchionna and S. Cozzini (with assistance from M. Venturoli and Antonella Luise), specifically to handle protein simulations. In agreement with the authors the package is also available from Daresbury Laboratory under the same terms as DL_POLY . Though having much in common with DL_POLY it represents a major rewrite, with many features not present in the original code (and with many original features missing). It is therefore documented separately from DL_POLY and users should consult the appropriate manual: "The DL-PROTEIN User Manual" by S. Melchionna and S. Cozzini [21], which also available from Daresbury Laboratory.

Our thanks go to S. Melchionna and S. Cozzini and their collaborators for generously making DLPROTEIN available to us and for extending that availablity to DL_POLY_2 users.

1.7 Other Information

The DL_POLY_2 web page: http://ftp.dl.ac.uk/TCS/Software/DL_POLY/main.html provides additional information in the form of

1. Access to all documentation (including licences);
2. Frequently asked questions;
3. Bug reports.

Daresbury Laboratory also maintains two DL_POLY_2 associated electronic mailing lists:

1. *dl_poly_news* - to which all registered DL_POLY_2 users are automatically subscribed. It is via this list that error reports and announcements of new versions are made. If you are a DL_POLY_2 user, but not on this list you may request to be added. Contact w.smith@dl.ac.uk.
2. *dl_poly_mail* - is a group list which is available to DL_POLY_2 users by request. Its purpose is to allow DL_POLY_2 users to broadcast information and queries to each other. To subscribe to this list send a mail message to majordomo@dl.ac.uk with the one-line message:

   subscribe dl_poly_mail

   Subsequent messages may be broadcast by e-mailing to the address: dl_poly_mail@dl.ac.uk.

Chapter 2

DL_POLY_2 Force Fields and Algorithms

Scope of Chapter

This chapter describes the interaction potentials and simulation algorithms coded into DL_POLY_2 .

2.1 The DL_POLY_2 Force Field

The force field is the set of functions needed to define the interactions in a molecular system. These may have a wide variety of analytical forms, with some basis in chemical physics, which must be parameterised to give the correct energy and forces. A huge variety of forms is possible and for this reason the DL_POLY_2 force field is designed to be adaptable. While it is not supplied with its own force field parameters, many of the functions familiar to GROMOS [3] DREIDING [7] and AMBER [4] users have been coded in the package, as well as less familiar forms. In addition DL_POLY_2 retains the possibility of the user defining additional potentials.

In DL_POLY_2 the total configuration energy of a molecular system may be written as:

$$\begin{aligned} U(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N) \;=\; & \sum_{i_{bond}=1}^{N_{bond}} U_{bond}(i_{bond}, \underline{r}_a, \underline{r}_b) \\ & + \sum_{i_{angle}=1}^{N_{angle}} U_{angle}(i_{angle}, \underline{r}_a, \underline{r}_b, \underline{r}_c) \\ & + \sum_{i_{dihed}=1}^{N_{dihed}} U_{dihed}(i_{dihed}, \underline{r}_a, \underline{r}_b, \underline{r}_c, \underline{r}_d) \\ & + \sum_{i_{inv}=1}^{N_{inv}} U_{inv}(i_{inv}, \underline{r}_a, \underline{r}_b, \underline{r}_c, \underline{r}_d) \\ & + \sum_{i=1}^{N-1} \sum_{j>i}^{N} U_{pair}(i, j, |\underline{r}_i - \underline{r}_j|) \\ & + \sum_{i=1}^{N-2} \sum_{j>i}^{N-1} \sum_{k>j}^{N} U_{3_body}(i, j, k, \underline{r}_i, \underline{r}_j, \underline{r}_k) \\ & + \sum_{i=1}^{N-3} \sum_{j>i}^{N-2} \sum_{k>j}^{N-1} \sum_{n>k}^{N} U_{4_body}(i, j, k, n, \underline{r}_i, \underline{r}_j, \underline{r}_k, \underline{r}_n) \\ & + \sum_{i=1}^{N} U_{extn}(i, \underline{r}_i, \underline{v}_i) \end{aligned} \tag{2.1}$$

where U_{bond}, U_{angle}, U_{dihed}, U_{inv}, U_{pair}, U_{3_body} and U_{4_body} are empirical interaction functions representing chemical bonds, valence angles, dihedral angles, inversion angles, pair-body, three-body and four-body forces respectively. The first four are regarded by DL_POLY_2 as *intra*-molecular interactions and the next three as *inter*-molecular interactions. The final term U_{extn} represents an *external field* potential. The position vectors $\underline{r}_a, \underline{r}_b, \underline{r}_c$ and $\underline{r}_d$ refer to the positions of the atoms specifically involved in a given interaction. (Almost universally, it is the *differences* in position that determine the interaction.) The numbers N_{bond}, N_{angle}, N_{dihed} and N_{inv} refer to the total numbers of these respective interactions present in the simulated system, and the indices i_{bond}, i_{angle}, i_{inv} and i_{dihed} uniquely specify an individual interaction of each type. It is important to note that there is

no global specification of the intramolecular interactions in DL_POLY_2 - all bonds, valence angles and dihedrals must be individually cited.

The indices i, j (and k, n) appearing in the pair-body (and three or four-body) terms indicate the atoms involved in the interaction. There is normally a very large number of these and they are therefore specified according to atom *types* rather than indices. In DL_POLY_2 it is assumed that the pair-body terms arise from van der Waals and/or electrostatic (Coulombic) forces. The former are regarded as short ranged interactions and the latter as long ranged. Long range forces require special techniques to evaluate accurately (see section 2.4.) In DL_POLY_2 the three-body terms are restricted to valence angle and H-bond forms. The nonbonded, three-body and four-body interactions are globally specified according to the *types* of atoms involved. DL_POLY_2 also has the ability to handle metals via density dependent functions (see below). Though essentially many-body potentials they are handled in DL_POLY_2 as special forms of pair potential.

In DL_POLY_2 the intramolecular bonded terms are handled using bookkeeping arrays, which specify the atoms involved in a particular interaction and point to the appropriate arrays of parameters that define the potential. The calculation of bonded forces therefore follows the simple scheme:

1. Every atom in the simulated system is assigned a unique index number from 1 to N;
2. Every intramolecular bonded term U_{type} in the system has a unique index number i_{type}: from 1 to N_{type} where *type* represents a bond, angle or dihedral.
3. A pointer array $key_{type}(n_{type}, i_{type})$ carries the indices of the specific atoms involved in the potential term labelled i_{type}. The dimension n_{type} will be 2, 3 or 4, if the term represents a bond, valence angle, dihedral/inversion.
4. The array $key_{type}(n_{type}, i_{type})$ is used to identify the atoms in a bonded term and the appropriate form of interaction and thus to calculate the energy and forces.

DL_POLY_2 calculates the nonbonded pair interactions using a Verlet neighbour list [10] which is reconstructed at intervals during the simulation. This list records the indices of all 'secondary' atoms within a certain radius of each 'primary' atom; the radius being the cut-off radius (r_{cut}) normally applied to the nonbonded potential function, plus an additional increment (Δr_{cut}). The neighbour list removes the need to scan over all atoms in the simulation at every timestep. The larger radius ($r_{cut} + \Delta r_{cut}$) means the same list can be used for several timesteps without requiring an update. The frequency at which the list must be updated depends on the thickness of the region Δr_{cut}. DL_POLY_2 has two methods for constructing the neighbour list: the first is based on the Brode-Ahlrichs scheme [22] and is used when r_{cut} is large in comparison with the simulation cell; the second uses the link-cell algorithm [23] when r_{cut} is relatively small. The potential energy and forces arising from the nonbonded interactions are calculated using interpolation tables.

A complication in the construction of the Verlet neighbour list for macromolecules is the concept of *excluded atoms*, which arises from the need to exclude certain atom pairs from the overall list. Which atom pairs need to be excluded is dependent on the precise

nature of the force field model, but as a minimum atom pairs linked via extensible bonds or constraints and atoms (grouped in pairs) linked via valence angles are probable candidates. The assumption behind this requirement is that atoms that are formally bonded in a chemical sense, should not participate in nonbonded interactions. (However this is not a universal requirement of all force fields.) The same considerations are needed in dealing with charged excluded atoms.DL_POLY_2 has several subroutines available for constructing the Verlet neighbour list, while taking care of the excluded atoms (see chapters 3 and 7 for further information.)

Three- and four-body nonbonded forces are assumed to be short ranged and therefore calculated using the link-cell algorithm [23]. They ignore the possibility of there being any excluded interactions involving the atoms concerned.

Throughout this section the description of the force field assumes the simulated system is described as an assembly of atoms. This is for convenience only and readers should understand that DL_POLY_2 does recognise molecular entities, defined either through constraint bonds or rigid bodies. In the case of rigid bodies, the atomic forces are resolved into molecular forces and torques. These matters are discussed in greater detail later in sections 2.5.1 and 2.5.6).

Note that the subroutines mentioned in the subsections of this chapter are described in greater detail in chapter 7.

2.2 The Intramolecular Potential Functions

In this section we catalogue and describe the forms of potential function available in DL_POLY_2 The **key words** required to select potential forms are given in brackets () before each definition. The derivations of the atomic forces, virial and stress tensor are also outlined.

2.2.1 Bond Potentials

The interatomic bond vector.

The bond potentials describe *explicit* bonds between specified atoms. They are functions of the interatomic distance only. The potential functions available are as follows.

1. Harmonic bond: (**harm**)

$$U(r_{ij}) = \frac{1}{2}k(r_{ij} - r_o)^2; \tag{2.2}$$

2. Morse potential: (**mors**)

$$U(r_{ij}) = E_o[\{1 - \exp(-k(r_{ij} - r_o))\}^2 - 1]; \tag{2.3}$$

3. 12-6 potential bond: (**12-6**)

$$U(r_{ij}) = \left(\frac{A}{r_{ij}^{12}}\right) - \left(\frac{B}{r_{ij}^{6}}\right); \tag{2.4}$$

4. Restrained harmonic: (**rhrm**)

$$U(r_{ij}) = \frac{1}{2}k(r_{ij} - r_o)^2 \qquad |r_{ij} - r_o| \leq r_c; \tag{2.5}$$

$$U(r_{ij}) = \frac{1}{2}kr_c^2 + kr_c(|r_{ij} - r_o| - r_c) \qquad |r_{ij} - r_o| > r_c; \tag{2.6}$$

5. Quartic potential: (**quar**)

$$U(r_{ij}) = \frac{k}{2}(r_{ij} - r_o)^2 + \frac{k'}{3}(r_{ij} - r_o)^3 + \frac{k''}{4}(r_{ij} - r_o)^4. \tag{2.7}$$

In these formulae r_{ij} is the distance between atoms labelled i and j:

$$r_{ij} = |\underline{r}_j - \underline{r}_i|, \tag{2.8}$$

where $\underline{r}_\ell$ is the position vector of an atom labelled ℓ. [1]

The force on the atom j arising from a bond potential is obtained using the general formula:

$$\underline{f}_j = -\frac{1}{r_{ij}}\left[\frac{\partial}{\partial r_{ij}}U(r_{ij})\right]\underline{r}_{ij}, \tag{2.9}$$

The force $\underline{f}_i$ acting on atom i is the negative of this.

The contribution to be added to the atomic virial is given by

$$\mathcal{W} = -\underline{r}_{ij} \cdot \underline{f}_j, \tag{2.10}$$

with only *one* such contribution from each bond.

The contribution to be added to the atomic stress tensor is given by

$$\sigma^{\alpha\beta} = r_{ij}^{\alpha} f_j^{\beta}, \tag{2.11}$$

where α and β indicate the x, y, z components. The atomic stress tensor derived in this way is symmetric.

In DL_POLY_2 bond forces are handled by the routine BNDFRC.

[1] Note: some DL_POLY_2 routines may use the convention that $\underline{r_{ij}} = \underline{r}_i - \underline{r}_j$.

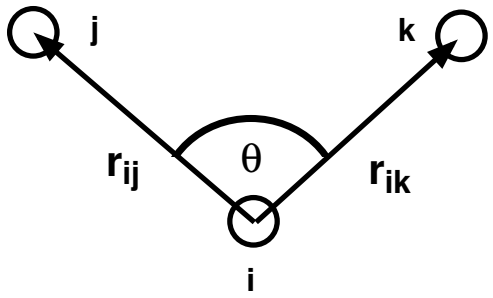
2.2.2 Distance Restraints

In DL_POLY_2 distance restraints, in which the separation between two atoms, is maintained around some preset value r_0 is handled as a special case of bond potentials. As a consequence distance restraints may be applied only between atoms in the same molecule. Unlike with application of the "pure" bond potentials, the electrostatic and van der Waals interactions between the pair of atoms are still evaluated when distance restraints are applied. All the potential forms of the previous section are avaliable as distance restraints, although they have different key words:

1. Harmonic potential: (**-hrm**)
2. Morse potential: (**-mrs**)
3. 12-6 potential bond: (**-126**)
4. Restrained harmonic: (**-rhm**)
5. Quartic potential: (**-qur**)

In DL_POLY_2 distance restraints are handled by the routine BNDFRC.

2.2.3 Valence Angle Potentials



The valence angle and associated vectors

The valence angle potentials describe the bond bending terms between the specified atoms. They should not be confused with the three body potentials described later, which are defined by atom types rather than indices.

1. Harmonic: (**harm**)
$$U(\theta_{jik}) = \frac{k}{2}(\theta_{jik} - \theta_0)^2; \tag{2.12}$$
2. Quartic: (**quar**)
$$U(\theta_{jik}) = \frac{k}{2}(\theta_{jik} - \theta_0)^2 + \frac{k'}{3}(\theta_{jik} - \theta_0)^3 + \frac{k''}{4}(\theta_{jik} - \theta_0)^4; \tag{2.13}$$

3. Truncated harmonic: (**thrm**)

$$U(\theta_{jik}) = \frac{k}{2}(\theta_{jik} - \theta_0)^2 \exp[-(r_{ij}^8 + r_{ik}^8)/\rho^8]; \tag{2.14}$$

4. Screened harmonic: (**shrm**)

$$U(\theta_{jik}) = \frac{k}{2}(\theta_{jik} - \theta_0)^2 \exp[-(r_{ij}/\rho_1 + r_{ik}/\rho_2)]; \tag{2.15}$$

5. Screened Vessal[24]: (**bvs1**)

$$\begin{aligned} U(\theta_{jik}) &= \frac{k}{8(\theta_{jik} - \pi)^2} \left\{ \left[(\theta_0 - \pi)^2 - (\theta_{jik} - \pi)^2 \right]^2 \right\} \\ &\quad \exp[-(r_{ij}/\rho_1 + r_{ik}/\rho_2)]; \end{aligned} \tag{2.16}$$

6. Truncated Vessal[25]: (**bvs2**)

$$\begin{aligned} U(\theta_{jik}) &= k[\theta_{jik}^a(\theta_{jik} - \theta_0)^2(\theta_{jik} + \theta_0 - 2\pi)^2 - \frac{a}{2}\pi^{a-1} \\ &\quad (\theta_{jik} - \theta_0)^2(\pi - \theta_0)^3] \exp[-(r_{ij}^8 + r_{ik}^8)/\rho^8]. \end{aligned} \tag{2.17}$$

7. Harmonic cosine: (**hcos**)

$$U(\theta_{jik}) = \frac{k}{2}(cos(\theta_{jik}) - cos(\theta_0))^2 \tag{2.18}$$

8. Cosine: (**cos**)

$$U(\theta_{jik}) = A[1 + cos(m\theta_{jik} - \delta)] \tag{2.19}$$

In these formulae θ_{jik} is the angle between bond vectors $\underline{r}_{ij}$ and $\underline{r}_{ik}$:

$$\theta_{jik} = cos^{-1}\left\{ \frac{\underline{r}_{ij} \cdot \underline{r}_{ik}}{r_{ij} r_{ik}} \right\} \tag{2.20}$$

In DL_POLY_2 the most general form for the valence angle potentials can be written as:

$$U(\theta_{jik}, r_{ij}, r_{ik}) = A(\theta_{jik}) S(r_{ij}) S(r_{ik}) \tag{2.21}$$

where $A(\theta)$ is a purely angular function and $S(r)$ is a screening or truncation function. All the function arguments are scalars. With this reduction the force on an atom derived from the valence angle potential is given by:

$$f_\ell^\alpha = -\frac{\partial}{\partial r_\ell^\alpha} U(\theta_{jik}, r_{ij}, r_{ik}), \tag{2.22}$$

with atomic label ℓ being one of i, j, k and α indicating the x, y, z component. The derivative is

$$\begin{aligned} -\frac{\partial}{\partial r_\ell^\alpha}U(\theta_{jik}, r_{ij}, r_{ik}) &= -S(r_{ij})S(r_{ik})\frac{\partial}{\partial r_\ell^\alpha}A(\theta_{jik}) \\ &\quad -A(\theta_{jik})S(r_{ik})(\delta_{\ell j}-\delta_{\ell i})\frac{r_{ij}^\alpha}{r_{ij}}\frac{\partial}{\partial r_{ij}}S(r_{ij}) \\ &\quad -A(\theta_{jik})S(r_{ij})(\delta_{\ell k}-\delta_{\ell i})\frac{r_{ik}^\alpha}{r_{ik}}\frac{\partial}{\partial r_{ik}}S(r_{ik}), \end{aligned} \tag{2.23}$$

with $\delta_{ab} = 1$ if $a = b$ and $\delta_{ab} = 0$ if $a \neq b$. In the absence of screening terms $S(r)$, this formula reduces to:

$$-\frac{\partial}{\partial r_\ell^\alpha}U(\theta_{jik}, r_{ij}, r_{ik}) = -\frac{\partial}{\partial r_\ell^\alpha}A(\theta_{jik}) \tag{2.24}$$

The derivative of the angular function is

$$-\frac{\partial}{\partial r_\ell^\alpha}A(\theta_{jik}) = \left\{\frac{1}{\sin(\theta_{jik})}\right\}\frac{\partial}{\partial\theta_{jik}}A(\theta_{jik})\frac{\partial}{\partial r_\ell^\alpha}\left\{\frac{\underline{r}_{ij}\cdot\underline{r}_{ik}}{r_{ij}r_{ik}}\right\}, \tag{2.25}$$

with

$$\begin{aligned} \frac{\partial}{\partial r_j^\alpha}\left\{\frac{\underline{r}_{ij}\cdot\underline{r}_{ik}}{r_{ij}r_{ik}}\right\} &= (\delta_{\ell j}-\delta_{\ell i})\frac{r_{ik}^\alpha}{r_{ij}r_{ik}} + (\delta_{\ell k}-\delta_{\ell i})\frac{r_{ij}^\alpha}{r_{ij}r_{ik}} - \\ &\quad \cos(\theta_{jik})\left\{(\delta_{\ell j}-\delta_{\ell i})\frac{r_{ij}^\alpha}{r_{ij}^2} + (\delta_{\ell k}-\delta_{\ell i})\frac{r_{ik}^\alpha}{r_{ik}^2}\right\} \end{aligned} \tag{2.26}$$

The atomic forces are then completely specified by the derivatives of the particular functions $A(\theta)$ and $S(r)$.

The contribution to be added to the atomic virial is given by

$$\mathcal{W} = -(\underline{r}_{ij}\cdot\underline{f}_j + \underline{r}_{ik}\cdot\underline{f}_k) \tag{2.27}$$

It is worth noting that in the absence of screening terms S(r), the virial is zero [26].

The contribution to be added to the atomic stress tensor is given by

$$\sigma^{\alpha\beta} = r_{ij}^\alpha f_j^\beta + r_{ik}^\alpha f_k^\beta \tag{2.28}$$

and the stress tensor is symmetric.

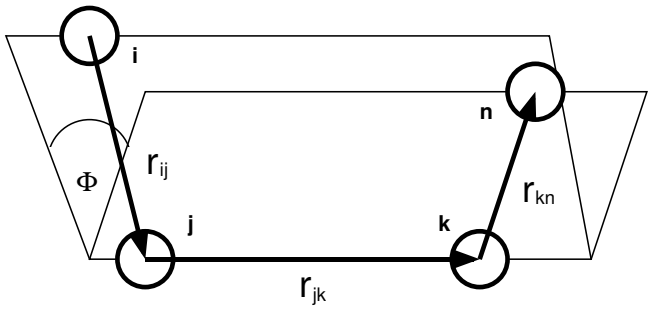
In DL_POLY_2 valence forces are handled by the routine ANGFRC.

2.2.4 Angular Restraints

In DL_POLY_2 angle restraints, in which the angle subtended by a triplet of atoms, is maintained around some preset value θ_0 is handled as a special case of angle potentials. As a consequence angle restraints may be applied only between atoms in the same molecule. Unlike with application of the "pure" angle potentials, the electrostatic and van der Waals interactions between the pair of atoms are still evaluated when distance restraints are applied. All the potential forms of the previous section are avaliable as angular restraints, although they have different key words:

1. Harmonic: (**-hrm**)
2. Quartic: (**-qur**)
3. Truncated harmonic: (**-thm**)
4. Screened harmonic: (**-shm**)
5. Screened Vessal[24]: (**-bv1**)
6. Truncated Vessal[25]: (**-bv2**)
7. Harmonic cosine: (**-hcs**)
8. Cosine : (**-cos**)

2.2.5 Dihedral Angle Potentials



The dihedral angle and associated vectors

The dihedral angle potentials describe the interaction arising from torsional forces in molecules. (They are sometimes referred to as torsion potentials.) They require the specification of four atomic positions. The potential functions available in DL_POLY_2 are as follows.

1. Cosine potential: (**cos**)

$$U(\phi_{ijkn}) = A\,[1 + \cos(m\phi_{ijkn} - \delta)] \tag{2.29}$$

2. Harmonic: (**harm**)

$$U(\phi_{ijkn}) = \frac{1}{2}k(\phi_{ijkn} - \phi_0)^2 \tag{2.30}$$

3. Harmonic cosine: (**hcos**)

$$U(\phi_{ijkn}) = \frac{k}{2}(cos(\phi_{ijkn}) - cos(\phi_0))^2 \tag{2.31}$$

4. Triple cosine: (**cos3**)

$$U(\phi) = \frac{1}{2}A_1(1 + cos(\phi)) + \frac{1}{2}A_2(1 - cos(2\phi)) + \frac{1}{2}A_3(1 + cos(3\phi)) \tag{2.32}$$

In these formulae ϕ_{ijkn} is the dihedral angle defined by

$$\phi_{ijkn} = \cos^{-1}\{B(\underline{r}_{ij}, \underline{r}_{jk}, \underline{r}_{kn})\}, \tag{2.33}$$

with

$$B(\underline{r}_{ij}, \underline{r}_{jk}, \underline{r}_{kn}) = \left\{ \frac{(\underline{r}_{ij} \times \underline{r}_{jk}) \cdot (\underline{r}_{jk} \times \underline{r}_{kn})}{|\underline{r}_{ij} \times \underline{r}_{jk}||\underline{r}_{jk} \times \underline{r}_{kn}|} \right\}. \tag{2.34}$$

With this definition, the sign of the dihedral angle is positive if the vector product $(\underline{r}_{ij} \times \underline{r}_{jk}) \times (\underline{r}_{jk} \times \underline{r}_{kn})$ is in the same direction as the bond vector $\underline{r}_{jk}$ and negative if in the opposite direction.

The force on an atom arising from the dihedral potential is given by

$$f_\ell^\alpha = -\frac{\partial}{\partial r_\ell^\alpha} U(\phi_{ijkn}), \tag{2.35}$$

with ℓ being one of i, j, k, n and α one of x, y, z. This may be expanded into

$$-\frac{\partial}{\partial r_\ell^\alpha} U(\phi_{ijkn}) = \left\{ \frac{1}{\sin(\phi_{ijkn})} \right\} \frac{\partial}{\partial \phi_{ijkn}} U(\phi_{ijkn}) \frac{\partial}{\partial r_\ell^\alpha} B(\underline{r}_{ij}, \underline{r}_{jk}, \underline{r}_{kn}). \tag{2.36}$$

The derivative of the function $B(\underline{r}_{ij}, \underline{r}_{jk}, \underline{r}_{kn})$ is

$$\begin{aligned} \frac{\partial}{\partial r_\ell^\alpha} B(\underline{r}_{ij}, \underline{r}_{jk}, \underline{r}_{kn}) &= \frac{1}{|\underline{r}_{ij} \times \underline{r}_{jk}||\underline{r}_{jk} \times \underline{r}_{kn}|} \frac{\partial}{\partial r_\ell^\alpha} \{(\underline{r}_{ij} \times \underline{r}_{jk}) \cdot (\underline{r}_{jk} \times \underline{r}_{kn})\} \\ &- \frac{\cos(\phi_{ijkn})}{2} \left\{ \frac{1}{|\underline{r}_{ij} \times \underline{r}_{jk}|^2} \frac{\partial}{\partial r_\ell^\alpha} |\underline{r}_{ij} \times \underline{r}_{jk}|^2 + \frac{1}{|\underline{r}_{jk} \times \underline{r}_{kn}|^2} \frac{\partial}{\partial r_\ell^\alpha} |\underline{r}_{jk} \times \underline{r}_{kn}|^2 \right\}, \end{aligned} \tag{2.37}$$

with

$$\begin{aligned} \frac{\partial}{\partial r_\ell^\alpha} \{(\underline{r}_{ij} \times \underline{r}_{jk}) \cdot (\underline{r}_{jk} \times \underline{r}_{kn})\} &= r_{ij}^\alpha ([\underline{r}_{jk}\underline{r}_{jk}]_\alpha (\delta_{\ell k} - \delta_{\ell n}) + [\underline{r}_{jk}\underline{r}_{kn}]_\alpha (\delta_{\ell k} - \delta_{\ell j})) + \\ & r_{jk}^\alpha ([\underline{r}_{ij}\underline{r}_{jk}]_\alpha (\delta_{\ell n} - \delta_{\ell k}) + [\underline{r}_{jk}\underline{r}_{kn}]_\alpha (\delta_{\ell j} - \delta_{\ell i})) + \\ & r_{kn}^\alpha ([\underline{r}_{ij}\underline{r}_{jk}]_\alpha (\delta_{\ell k} - \delta_{\ell j}) + [\underline{r}_{jk}\underline{r}_{jk}]_\alpha (\delta_{\ell i} - \delta_{\ell j})) + \\ & 2r_{jk}^\alpha [\underline{r}_{ij}\underline{r}_{kn}]_\alpha (\delta_{\ell j} - \delta_{\ell k}), \end{aligned} \tag{2.38}$$

$$\begin{aligned} \frac{\partial}{\partial r_\ell^\alpha} |\underline{r}_{ij} \times \underline{r}_{jk}|^2 &= 2r_{ij}^\alpha ([\underline{r}_{jk}\underline{r}_{jk}]_\alpha (\delta_{\ell j} - \delta_{\ell i}) + [\underline{r}_{ij}\underline{r}_{jk}]_\alpha (\delta_{\ell j} - \delta_{\ell k})) + \\ & 2r_{jk}^\alpha ([\underline{r}_{ij}\underline{r}_{ij}]_\alpha (\delta_{\ell k} - \delta_{\ell j}) + [\underline{r}_{ij}\underline{r}_{jk}]_\alpha (\delta_{\ell i} - \delta_{\ell j})), \end{aligned} \tag{2.39}$$

$$\frac{\partial}{\partial r_\ell^\alpha}|\underline{r}_{jk}\times\underline{r}_{kn}|^2 = 2r_{kn}^\alpha([\underline{r}_{jk}\underline{r}_{jk}]_\alpha(\delta_{\ell n}-\delta_{\ell k})+[\underline{r}_{jk}\underline{r}_{kn}]_\alpha(\delta_{\ell j}-\delta_{\ell k}))+ 2r_{jk}^\alpha([\underline{r}_{kn}\underline{r}_{kn}]_\alpha(\delta_{\ell k}-\delta_{\ell j})+[\underline{r}_{jk}\underline{r}_{kn}]_\alpha(\delta_{\ell k}-\delta_{\ell n})). \quad (2.40)$$

Where we have used the the following definition:

$$[\underline{a}\ \underline{b}]_\alpha=\sum_\beta(1-\delta_{\alpha\beta})a^\beta b^\beta. \quad (2.41)$$

Formally, the contribution to be added to the atomic virial is given by

$$\mathcal{W}=-\sum_{i=1}^4\underline{r}_i\cdot\underline{f}_i \quad (2.42)$$

However it is possible to show (by tedious algebra using the above formulae, or more elegantly by thermodynamic arguments [26],) that the dihedral makes *no* contribution to the atomic virial.

The contribution to be added to the atomic stress tensor is given by

$$\sigma^{\alpha\beta} = r_{ij}^\alpha p_i^\beta+r_{jk}^\alpha p_{jk}^\beta+r_{kn}^\alpha p_n^\beta -\frac{\cos(\phi_{ijkn})}{2}\left\{r_{ij}^\alpha g_i^\beta+r_{jk}^\alpha g_k^\beta+r_{jk}^\alpha h_j^\beta+r_{kn}^\alpha h_n^\beta\right\}, \quad (2.43)$$

with

$$p_i^\alpha = (r_{jk}^\alpha[\underline{r}_{jk}\underline{r}_{kn}]_\alpha-r_{kn}^\alpha[\underline{r}_{jk}\underline{r}_{jk}]_\alpha)/(|\underline{r}_{ij}\times\underline{r}_{jk}||\underline{r}_{jk}\times\underline{r}_{kn}|) \quad (2.44)$$

$$p_n^\alpha = (r_{jk}^\alpha[\underline{r}_{ij}\underline{r}_{jk}]_\alpha-r_{ij}^\alpha[\underline{r}_{jk}\underline{r}_{jk}]_\alpha)/(|\underline{r}_{ij}\times\underline{r}_{jk}||\underline{r}_{jk}\times\underline{r}_{kn}|) \quad (2.45)$$

$$p_{jk}^\alpha = (r_{ij}^\alpha[\underline{r}_{jk}\underline{r}_{kn}]_\alpha+r_{kn}^\alpha[\underline{r}_{ij}\underline{r}_{jk}]_\alpha-2r_{jk}^\alpha[\underline{r}_{ij}\underline{r}_{kn}]_\alpha)/(|\underline{r}_{ij}\times\underline{r}_{jk}||\underline{r}_{jk}\times\underline{r}_{kn}|) \quad (2.46)$$

$$g_i^\alpha = 2(r_{ij}^\alpha[\underline{r}_{jk}\underline{r}_{jk}]_\alpha-r_{jk}^\alpha[\underline{r}_{ij}\underline{r}_{jk}]_\alpha)/|\underline{r}_{ij}\times\underline{r}_{jk}|^2 \quad (2.47)$$

$$g_k^\alpha = 2(r_{jk}^\alpha[\underline{r}_{ij}\underline{r}_{ij}]_\alpha-r_{ij}^\alpha[\underline{r}_{ij}\underline{r}_{jk}]_\alpha)/|\underline{r}_{ij}\times\underline{r}_{jk}|^2 \quad (2.48)$$

$$h_j^\alpha = 2(r_{jk}^\alpha[\underline{r}_{kn}\underline{r}_{kn}]_\alpha-r_{kn}^\alpha[\underline{r}_{jk}\underline{r}_{kn}]_\alpha)/|\underline{r}_{jk}\times\underline{r}_{kn}|^2 \quad (2.49)$$

$$h_n^\alpha = 2(r_{kn}^\alpha[\underline{r}_{kn}\underline{r}_{kn}]_\alpha-r_{jk}^\alpha[\underline{r}_{jk}\underline{r}_{kn}]_\alpha)/|\underline{r}_{jk}\times\underline{r}_{kn}|^2 \quad (2.50)$$

The sum of the diagonal elements of the stress tensor is zero (since the virial is zero) and the matrix is symmetric.

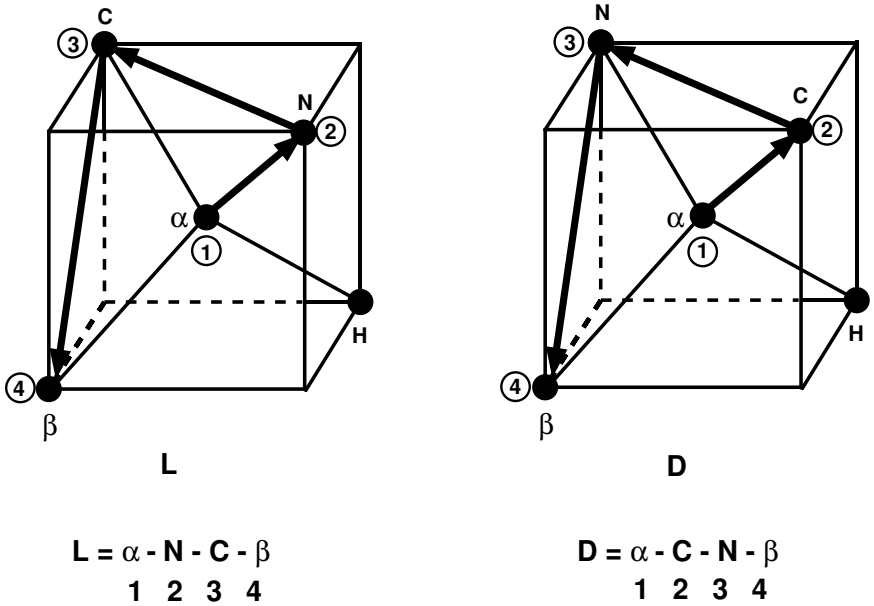
Lastly, it should be noted that the above description does not take into account the possible inclusion of distance-dependent 1-4 interactions, as permitted by some force fields. Such interactions are permissible in DL_POLY_2 and are described in the section on pair potentials below. DL_POLY_2 also permits scaling of the 1-4 interactions by a numerical factor. 1-4 interactions do, of course, contribute to the atomic virial.

In DL_POLY_2 dihedral forces are handled by the routine DIHFRC.

2.2.6 Improper Dihedral Angle Potentials

Improper dihedrals are used to restrict the geometry of molecules and as such need not have a simple relation to conventional chemical bonding. DL_POLY_2 makes no distinction between dihedral angle functions and improper dihedrals (both are calculated by the same subroutines) and all the comments made in the preceeding section apply.

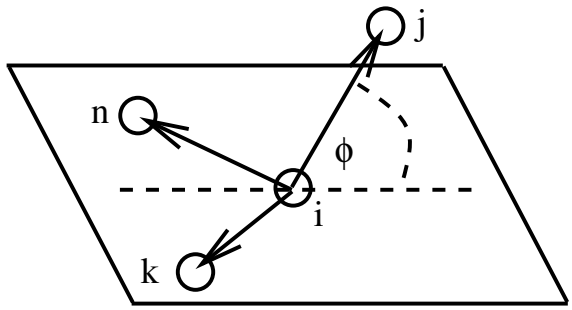
An important example of the use of the improper dihedral is to conserve the structure of chiral centres in molecules modelled by united-atom centres. For example α-amino acids such as alanine ($CH_3CH(NH_2)COOH$), in which it is common to represent the CH_3 and CH groups as single centres. Conservation of the chirality of the α carbon is achieved by defining a harmonic improper dihedral angle potential with an equilibrium angle of 35.264^o. The angle is defined by vectors $\underline{r}_{12}$, $\underline{r}_{23}$ and $\underline{r}_{34}$, where the atoms 1,2,3 and 4 are shown in the following figure. The figure defines the D and L enantiomers consistent with the international (IUPAC) convention. When defining the dihedral, the atom indices are entered in DL_POLY_2 in the order 1-2-3-4.



The L and D enantiomers and defining vectors

In DL_POLY_2 improper dihedral forces are handled by the routine DIHFRC.

2.2.7 Inversion Angle Potentials



The inversion angle and associated vectors

The inversion angle potentials describe the interaction arising from a particular geometry of three atoms around a central atom. The best known example of this is the arrangement of hydrogen atoms around nitrogen in ammonia to form a trigonal pyramid. The hydrogens can 'flip' like an inverting umbrella to an alternative structure, which in this case is identical, but in principle causes a change in chirality. The force restraining the ammonia to one structure can be described as an inversion potential (though it is usually augmented by valence angle potentials also). The inversion angle is defined in the figure above - **note that the inversion angle potential is a sum of the three possible inversion angle terms.** It resembles a dihedral potential in that it requires the specification of four atomic positions.

The potential functions available in DL_POLY_2 are as follows.

1. Harmonic: (**harm**)
$$U(\phi_{ijkn}) = \frac{1}{2}k(\phi_{ijkn} - \phi_0)^2 \tag{2.51}$$

2. Harmonic cosine: (**hcos**)
$$U(\phi_{ijkn}) = \frac{k}{2}(cos(\phi_{ijkn}) - cos(\phi_0))^2 \tag{2.52}$$

3. Planar potential: (**plan**)
$$U(\phi_{ijkn}) = A\,[1 - \cos(\phi_{ijkn})] \tag{2.53}$$

In these formulae ϕ_{ijkn} is the inversion angle defined by

$$\phi_{ijkn} = \cos^{-1}\left\{\frac{\underline{r}_{ij}\cdot\underline{w}_{kn}}{r_{ij}w_{kn}}\right\}, \tag{2.54}$$

with

$$\underline{w}_{kn} = (\underline{r}_{ij}\cdot\hat{\underline{u}}_{kn})\hat{\underline{u}}_{kn} + (\underline{r}_{ij}\cdot\hat{\underline{v}}_{kn})\hat{\underline{v}}_{kn} \tag{2.55}$$

and the unit vectors

$$\begin{aligned}\hat{\underline{u}}_{kn} &= (\hat{\underline{r}}_{ik} + \hat{\underline{r}}_{in})/|\hat{\underline{r}}_{ik} + \hat{\underline{r}}_{in}| \\ \hat{\underline{v}}_{kn} &= (\hat{\underline{r}}_{ik} - \hat{\underline{r}}_{in})/|\hat{\underline{r}}_{ik} - \hat{\underline{r}}_{in}|.\end{aligned} \tag{2.56}$$

As usual, $\underline{r}_{ij} = \underline{r}_j - \underline{r}_i$ *etc.* and the hat $\hat{\underline{r}}$ indicates a *unit* vector in the direction of $\underline{r}$. The total inversion potential requires the calculation of three such angles, the formula being derived from the above using the cyclic permutation of the indices $j \to k \to n \to j$ *etc.*

Equivalently, the angle ϕ_{ijkn} may be written as

$$\phi_{ijkn} = \cos^{-1}\left\{\frac{[(\underline{r}_{ij}\cdot\hat{\underline{u}}_{kn})^2 + (\underline{r}_{ij}\cdot\hat{\underline{v}}_{kn})^2]^{1/2}}{r_{ij}}\right\} \tag{2.57}$$

Formally, the force on an atom arising from the inversion potential is given by

$$f_\ell^\alpha = -\frac{\partial}{\partial r_\ell^\alpha}U(\phi_{ijkn}), \tag{2.58}$$

with ℓ being one of i,j,k,n and α one of x,y,z. This may be expanded into

$$\begin{aligned} -\frac{\partial}{\partial r_\ell^\alpha}U(\phi_{ijkn}) &= \left\{\frac{1}{\sin(\phi_{ijkn})}\right\}\frac{\partial}{\partial\phi_{ijkn}}U(\phi_{ijkn})\times \\ &\quad \frac{\partial}{\partial r_\ell^\alpha}\left\{\frac{[(\underline{r}_{ij}\cdot\hat{\underline{u}}_{kn})^2 + (\underline{r}_{ij}\cdot\hat{\underline{v}}_{kn})^2]^{1/2}}{r_{ij}}\right\}. \end{aligned} \tag{2.59}$$

Following through the (extremely tedious!) differentiation gives the result:

$$\begin{aligned} f_\ell^\alpha &= \left\{\frac{1}{\sin(\phi_{ijkn})}\right\}\frac{\partial}{\partial\phi_{ijkn}}U(\phi_{ijkn})\times \\ &\left\{-(\delta_{\ell j}-\delta_{\ell i})\frac{cos(\phi_{ijkn})}{r_{ij}^2}r_{ij}^\alpha + \frac{1}{r_{ij}w_{kn}}\left[(\delta_{\ell j}-\delta_{\ell i})\{(\underline{r}_{ij}\cdot\hat{\underline{u}}_{kn})\hat{u}_{kn}^\alpha + (\underline{r}_{ij}\cdot\hat{\underline{v}}_{kn})\hat{v}_{kn}^\alpha\}\right.\right. \\ &+(\delta_{\ell k}-\delta_{\ell i})\frac{\underline{r}_{ij}\cdot\hat{\underline{u}}_{kn}}{u_{kn}r_{ik}}\left\{r_{ij}^\alpha - (\underline{r}_{ij}\cdot\hat{\underline{u}}_{kn})\hat{u}_{kn}^\alpha - (\underline{r}_{ij}\cdot\underline{r}_{ik} - (\underline{r}_{ij}\cdot\hat{\underline{u}}_{kn})(\underline{r}_{ik}\cdot\hat{\underline{u}}_{kn}))\frac{r_{ik}^\alpha}{r_{ik}^2}\right\} \\ &+(\delta_{\ell k}-\delta_{\ell i})\frac{\underline{r}_{ij}\cdot\hat{\underline{v}}_{kn}}{v_{kn}r_{ik}}\left\{r_{ij}^\alpha - (\underline{r}_{ij}\cdot\hat{\underline{v}}_{kn})\hat{v}_{kn}^\alpha - (\underline{r}_{ij}\cdot\underline{r}_{ik} - (\underline{r}_{ij}\cdot\hat{\underline{v}}_{kn})(\underline{r}_{ik}\cdot\hat{\underline{v}}_{kn}))\frac{r_{ik}^\alpha}{r_{ik}^2}\right\} \\ &+(\delta_{\ell n}-\delta_{\ell i})\frac{\underline{r}_{ij}\cdot\hat{\underline{u}}_{kn}}{u_{kn}r_{in}}\left\{r_{ij}^\alpha - (\underline{r}_{ij}\cdot\hat{\underline{u}}_{kn})\hat{u}_{kn}^\alpha - (\underline{r}_{ij}\cdot\underline{r}_{in} - (\underline{r}_{ij}\cdot\hat{\underline{u}}_{kn})(\underline{r}_{in}\cdot\hat{\underline{u}}_{kn}))\frac{r_{in}^\alpha}{r_{in}^2}\right\} \\ &\left.\left.+(\delta_{\ell n}-\delta_{\ell i})\frac{\underline{r}_{ij}\cdot\hat{\underline{v}}_{kn}}{v_{kn}r_{in}}\left\{r_{ij}^\alpha - (\underline{r}_{ij}\cdot\hat{\underline{v}}_{kn})\hat{v}_{kn}^\alpha - (\underline{r}_{ij}\cdot\underline{r}_{in} - (\underline{r}_{ij}\cdot\hat{\underline{v}}_{kn})(\underline{r}_{in}\cdot\hat{\underline{v}}_{kn}))\frac{r_{in}^\alpha}{r_{in}^2}\right\}\right]\right\} \end{aligned} \tag{2.60}$$

This general formula applies to all atoms $\ell = i,j,k,n$. It must be remembered however, that these formulae apply to just one of the three contributing terms (i.e. one angle ϕ) of the full inversion potential: specifically the inversion angle pertaining to the out-of-plane vector $\underline{r}_{ij}$. The contributions arising from the other vectors $\underline{r}_{ik}$ and $\underline{r}_{in}$ are obtained by the cyclic permutation of the indices in the manner described above. All these force contributions must be added to the final atomic forces.

Formally, the contribution to be added to the atomic virial is given by

$$\mathcal{W} = -\sum_{i=1}^{4}\underline{r}_i\cdot\underline{f}_i \tag{2.61}$$

However it is possible to show by thermodynamic arguments (*cf* [26],) or simply from the fact that the sum of forces on atoms j,k and n is equal and opposite to the force on atom i, that the inversion potential makes *no* contribution to the atomic virial.

If the force components f_ℓ^α for atoms $\ell = i, j, k, n$ are calculated using the above formulae, it is easily seen that the contribution to be added to the atomic stress tensor is given by

$$\sigma^{\alpha\beta} = r_{ij}^\alpha f_j^\beta + r_{ik}^\alpha f_k^\beta + r_{in}^\alpha f_n^\beta \tag{2.62}$$

The sum of the diagonal elements of the stress tensor is zero (since the virial is zero) and the matrix is symmetric.

In DL_POLY_2 inversion forces are handled by the routine INVFRC.

2.2.8 Tethering Forces

DL_POLY_2 also allows atomic sites to be tethered to a fixed point in space, $\underline{r}_0$ taken as their position at the beginning of the simulation. This is also known as position restraining. The specification, which comes as part of the molecular description, requires a tether potential type and the associated interaction parameters.

Note, firstly, that application of tethering potentials means that momentum will no longer be a conserved quantity of the simulation. Secondly, in constant pressure simulations, where the MD cell changes size or shape, the reference position is scaled with the cell vectors.

The potential functions available in DL_POLY_2 are as follows, in each case r_{i0} is the distance of the atom from its position at $t = 0$:

1. harmonic potential: (**harm**)
$$U(r_{i0}) = \frac{1}{2}k(r_{i0})^2; \tag{2.63}$$

2. restrained harmonic :(**rhrm**)
$$U(r_{i0}) = \frac{1}{2}k(r_{i0})^2 \qquad r_{i0} \le r_c; \tag{2.64}$$
$$U(r_{i0}) = \frac{1}{2}kr_c^2 + kr_c(r_{i0} - r_c) \qquad r_{i0} > r_c; \tag{2.65}$$

3. Quartic potential: (**quar**)
$$U(r_{i0}) = \frac{k}{2}(r_{i0})^2 + \frac{k'}{3}(r_{i0})^3 + \frac{k''}{4}(r_{i0})^4. \tag{2.66}$$

The force on the atom i arising from a tether potential is obtained using the general formula:

$$\underline{f}_i = -\frac{1}{r_{i0}}\left[\frac{\partial}{\partial r_{i0}}U(r_{i0})\right]\underline{r}_{i0}, \tag{2.67}$$

The contribution to be added to the atomic virial is given by

$$\mathcal{W} = \underline{r}_{i0} \cdot \underline{f}_i, \tag{2.68}$$

The contribution to be added to the atomic stress tensor is given by

$$\sigma^{\alpha\beta} = -r_{i0}^{\alpha} f_i^{\beta}, \tag{2.69}$$

where α and β indicate the x, y, z components. The atomic stress tensor derived in this way is symmetric.

In DL_POLY_2 bond forces are handled by the routine TETHFRC.

2.2.9 Frozen Atoms

DL_POLY_2 also allows atoms to be completely immobilised (*i.e.* "frozen" at a fixed point in the MD cell). This is achieved by setting all forces and velocities associated with that atom to zero during each MD timestep. Frozen atoms are signalled by assigning an atom a non-zero value for the freeze parameter in the FIELD file. DL_POLY_2 does not calculate contributions to the virial or the stress tensor arising from the constraints required to freeze atomic positions. In DL_POLY_2 the frozen atom option cannot be used for sites in a rigid body. As with the tethering potential, the reference position is scaled with the cell vectors in constant pressure simulations.

In DL_POLY_2 the frozen atom option is handled by the subroutine FREEZE.

2.3 The Intermolecular Potential Functions

In this section we outline the pair-body, three-body and four-body potential functions available in DL_POLY_2 . An important distinction between these and intramolecular (bond) forces in DL_POLY_2 is that they are specified by *atom types* rather than atom indices.

2.3.1 Short Ranged (van der Waals) Potentials

The short ranged pair forces available in DL_POLY_2 are as follows.

1. 12 - 6 potential: (**12-6**)
$$U(r_{ij}) = \left(\frac{A}{r_{ij}^{12}}\right) - \left(\frac{B}{r_{ij}^{6}}\right); \tag{2.70}$$

2. Lennard-Jones: (**lj**)
$$U(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right]; \tag{2.71}$$

3. n - m potential [27]: (**nm**)
$$U(r_{ij}) = \frac{E_o}{(n-m)} \left[m\left(\frac{r_o}{r_{ij}}\right)^{n} - n\left(\frac{r_o}{r_{ij}}\right)^{m}\right]; \tag{2.72}$$

4. Buckingham potential: (**buck**)

$$U(r_{ij}) = A\ \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C}{r_{ij}^6}; \tag{2.73}$$

5. Born-Huggins-Meyer potential: (**bhm**)

$$U(r_{ij}) = A\ \exp[B(\sigma - r_{ij})] - \frac{C}{r_{ij}^6} - \frac{D}{r_{ij}^8}; \tag{2.74}$$

6. Hydrogen-bond (12 - 10) potential: (**hbnd**)

$$U(r_{ij}) = \left(\frac{A}{r_{ij}^{12}}\right) - \left(\frac{B}{r_{ij}^{10}}\right); \tag{2.75}$$

7. Shifted force n - m potential [27]: (**snm**)

$$\begin{aligned} U(r_{ij}) &= \frac{\alpha E_o}{(n-m)}\left[m\beta^n\left\{\left(\frac{r_o}{r_{ij}}\right)^n - \left(\frac{1}{\gamma}\right)^n\right\} - n\beta^m\left\{\left(\frac{r_o}{r_{ij}}\right)^m - \left(\frac{1}{\gamma}\right)^m\right\}\right] \\ &\quad + \frac{nm\alpha E_o}{(n-m)}\left(\frac{r_{ij} - \gamma r_o}{\gamma r_o}\right)\left\{\left(\frac{\beta}{\gamma}\right)^n - \left(\frac{\beta}{\gamma}\right)^m\right\} \end{aligned} \tag{2.76}$$

with

$$\gamma = \frac{r_{cut}}{r_o} \tag{2.77}$$

$$\beta = \gamma\left(\frac{\gamma^{m+1} - 1}{\gamma^{n+1} - 1}\right)^{\frac{1}{n-m}} \tag{2.78}$$

$$\alpha = \frac{(n-m)}{[n\beta^m(1 + (m/\gamma - m - 1)/\gamma^m) - m\beta^n(1 + (n/\gamma - n - 1)/\gamma^n)]} \tag{2.79}$$

This peculiar form has the advantage over the standard shifted n-m potential in that both E_o and r_0 (well depth and location of minimum) retain their original meaning after the shifting process.

8. Tabulation: (**tab**). The potential is defined numerically only.

The parameters defining these potentials are supplied to DL_POLY_2 at run time (see the description of the FIELD file in section 4.1.3). Each atom type in the system is specified by a unique eight-character label defined by the user. The pair potential is then defined internally by the combination of two atom labels.

As well as the numerical parameters defining the potentials, DL_POLY_2 must also be provided with a cutoff radius r_{cut}, which sets a range limit on the computation of the interaction. Together with the parameters, the cutoff is used by the subroutine FORGEN (or FORGEN_RSQ) to construct an interpolation array `vvv` for the potential function over

the range 0 to r_{cut}. A second array ggg is also calculated, which is related to the potential via the formula:

$$G(r_{ij}) = -r_{ij}\frac{\partial}{\partial r_{ij}}U(r_{ij}), \tag{2.80}$$

and is used in the calculation of the forces. Both arrays are tabulated in units of energy. The use of interpolation arrays, rather than the explicit formulae, makes the routines for calculating the potential energy and atomic forces very general, and enables the use of user defined pair potential functions. DL_POLY_2 also allows the user to read in the interpolation arrays directly from a file (see the description of the FORTAB routine (chapter 7) and the TABLE file (section 4.1.5). This is particularly useful if the pair potential function has no simple analytical description (e.g. spline potentials).

The force on an atom j derived from one of these potentials is formally calculated with the standard formula:

$$\underline{f}_j = -\frac{1}{r_{ij}}\left[\frac{\partial}{\partial r_{ij}}U(r_{ij})\right]\underline{r}_{ij}, \tag{2.81}$$

where $\underline{r}_{ij} = \underline{r}_j - \underline{r}_i$. The force on atom i is the negative of this.

The contribution to be added to the atomic virial (for each pair interaction) is

$$\mathcal{W} = -\underline{r}_{ij} \cdot \underline{f}_j. \tag{2.82}$$

The contribution to be added to the atomic stress tensor is given by

$$\sigma^{\alpha\beta} = r_{ij}^{\alpha} f_j^{\beta}, \tag{2.83}$$

where α and β indicate the x, y, z components. The atomic stress tensor derived from the pair forces is symmetric.

Since the calculation of pair potentials assumes a spherical cutoff (r_{cut}) it is necessary to apply a *long range correction* to the system potential energy and virial. Explicit formulae are needed for each case and are derived as follows. For two atom types a and b, the correction for the potential energy is calculated via the integral

$$U_{corr}^{ab} = 2\pi\frac{N_a N_b}{V}\int_{r_{cut}}^{\infty} g_{ab}(r)U_{ab}(r)r^2 dr \tag{2.84}$$

where N_a, N_b are the numbers of atoms of types a and b, V is the system volume and $g_{ab}(r)$ and $U_{ab}(r)$ are the appropriate pair correlation function and pair potential respectively. It is usual to assume $g_{ab}(r) = 1$ for $r > r_{cut}$. DL_POLY_2 sometimes makes the additional assumption that the repulsive part of the short ranged potential is negligible beyond r_{cut}.

The correction for the system virial is

$$\mathcal{W}_{corr}^{ab} = -2\pi\frac{N_a N_b}{V}\int_{r_{cut}}^{\infty} g_{ab}(r)\frac{\partial}{\partial r}U_{ab}(r)r^3 dr, \tag{2.85}$$

where the same approximations are applied. Note that these formulae are based on the assumption that the system is reasonably isotropic beyond the cutoff.

In DL_POLY_2 the short ranged forces are calculated by one of the routines SRFRCE, SRFRCE_RSQ, and SRFRCENEU. The long range corrections are calculated by routine LRCORRECT. The calculation makes use of the Verlet neighbour list described above.

2.3.2 Metal Potentials

DL_POLY_2 includes density dependent potentials suitable for calculating the properties of metals. The basic model is due to Finnis and Sinclair [28] as implemented by Sutton and Chen [6]. The form of the potential is: (**stch**)

$$U_{sc} = \epsilon \left[\sum_{i<j} \left(\frac{a}{r_{ij}} \right)^n - C \sum_i \rho_i^{1/2} \right], \tag{2.86}$$

where the *local density* ρ_i is given by

$$\rho_i = \sum_j \left(\frac{a}{r_{ij}} \right)^m \tag{2.87}$$

The Sutton-Chen potential has the advantage that it is decomposable into pair contributions and thus falls within the general tabulation scheme of DL_POLY_2 , where it is treated as a short ranged interaction. The same form of potential may be used in alloys, through the appropriate choice of parameters ϵ and a. The parameters n and m however must be the same for all component elements. DL_POLY_2 calculates this potential in two stages: the first calculates the local density ρ_i for each atom; and the second calculates the potential energy and forces. Interpolation arrays are used in both these stages.

The total force $\underline{f}_j^{tot}$ on an atom j derived from this potential is calculated in the standard way:

$$\underline{f}_j^{tot} = -\underline{\nabla}_j U_{sc}, \tag{2.88}$$

which gives

$$\underline{f}_j^{tot} = -\epsilon \sum_{i \neq j} \left[n \left(\frac{a}{r_{ij}} \right)^n - \frac{Cm}{2} (\rho_j^{-1/2} + \rho_i^{-1/2}) \left(\frac{a}{r_{ij}} \right)^m \right] \left(\frac{1}{r_{ij}^2} \right) \underline{r_{ij}}, \tag{2.89}$$

which is recognisable as a sum of pair forces, for example the force on atom j due to the atom i:

$$\underline{f}_j = -\epsilon \left[n \left(\frac{a}{r_{ij}} \right)^n - \frac{Cm}{2} (\rho_j^{-1/2} + \rho_i^{-1/2}) \left(\frac{a}{r_{ij}} \right)^m \right] \left(\frac{1}{r_{ij}^2} \right) \underline{r_{ij}}, \tag{2.90}$$

where $\underline{r}_{ij} = \underline{r}_j - \underline{r}_i$. The force on atom i is the negative of this.

With the pair forces thus defined the contribution to be added to the atomic virial *from each atom pair* is then

$$\mathcal{W} = -\underline{r}_{ij} \cdot \underline{f}_j. \tag{2.91}$$

The contribution to be added to the atomic stress tensor is given by

$$\sigma^{\alpha\beta} = r_{ij}^{\alpha} f_j^{\beta}, \tag{2.92}$$

where α and β indicate the x, y, z components. The atomic stress tensor is symmetric.

The long range correction for the system potential is in two parts. Firstly by analogy with the short ranged potentials the correction to the local density is obtained by

$$\rho_i = \rho_i^o + 4\pi\bar{\rho}\int_{r_{cut}}^{\infty}\left(\frac{a}{r}\right)^m r^2 dr, \tag{2.93}$$

where ρ_i^o is the uncorrected local density and $\bar{\rho}$ is the *mean particle density*. Evaluating the integral yields

$$\delta\rho = 4\pi\frac{\bar{\rho}a^3}{(m-3)}\left(\frac{a}{r_{cut}}\right)^{m-3} \tag{2.94}$$

which is the local density correction and is identical for all atoms. The correction is applied immediately after the local density is calculated. The density term of the Sutton Chen potential needs no further correction. The pair term correction is obtained by analogy with the short ranged potentials and is

$$U_{corr} = 2\pi\frac{N\epsilon\bar{\rho}a^3}{(n-3)}\left(\frac{a}{r_{cut}}\right)^{n-3}. \tag{2.95}$$

The correction to the local density having already been applied.

To estimate the virial correction we assume the corrected local densities are constants (i.e. independent of distance - at least beyond the range r_{cut}). This allows the virial correction to be computed by the methods used in the short ranged potentials. The result is:

$$\mathcal{W}_{corr} = -2\pi\bar{\rho}a^3\left\{\frac{nN\epsilon}{(n-3)}\left(\frac{a}{r_{cut}}\right)^{n-3} - \frac{m\epsilon^2C^2}{(m-3)}\left(\frac{a}{r_{cut}}\right)^{m-3}\sum_i^N \rho_i^{-1/2}\right\} \tag{2.96}$$

This correction may be used as it stands, or with the further approximation:

$$\sum_i^N \rho_i^{-1/2} = \frac{N}{<\rho_i^{1/2}>} \tag{2.97}$$

where $<\rho_i^{1/2}>$ is regarded as a constant of the system.

In DL_POLY_2 the metal forces are handled by the routine SUTTCHEN. The local density is calculated by routines SCDENS and DENLOC. The long range corrections are calculated by LRCMETAL.

2.3.3 Three Body Potentials

The three-body potentials in DL_POLY_2 are mostly valence angle forms. (They are primarily included to permit simulation of amorphous materials e.g. silicate glasses.) However, these have been extended to include the DREIDING [7] hydrogen bond. The potential forms available are as follows.

1. Truncated harmonic: (**thrm**)

$$U(\theta_{jik}) = \frac{k}{2}(\theta_{jik}-\theta_0)^2\exp[-(r_{ij}^8+r_{ik}^8)/\rho^8]; \tag{2.98}$$

2. Screened Harmonic: (**shrm**)

$$U(\theta_{jik}) = \frac{k}{2}(\theta_{jik} - \theta_0)^2 \exp[-(r_{ij}/\rho_1 + r_{ik}/\rho_2)]; \tag{2.99}$$

3. Screened Vessal[24]: (**bvs1**)

$$\begin{aligned} U(\theta_{jik}) &= \frac{k}{8(\theta_{jik} - \pi)^2} \left\{ \left[(\theta_0 - \pi)^2 - (\theta_{jik} - \pi)^2 \right]^2 \right\} \\ &\quad \exp[-(r_{ij}/\rho_1 + r_{ik}/\rho_2)]; \end{aligned} \tag{2.100}$$

4. Truncated Vessal[25]: (**bvs2**)

$$\begin{aligned} U(\theta_{jik}) &= k[\theta_{jik}^a(\theta_{jik} - \theta_0)^2(\theta_{jik} + \theta_0 - 2\pi)^2 - \frac{a}{2}\pi^{a-1} \\ &\quad (\theta_{jik} - \theta_0)^2(\pi - \theta_0)^3] \exp[-(r_{ij}^8 + r_{ik}^8)/\rho^8]. \end{aligned} \tag{2.101}$$

5. DREIDING hydrogen bond [7]: (**hbnd**

$$U(\theta_{jik}) = D_{hb} cos^4(\theta_{jik})[5(R_{hb}/r_{jk})^{12} - 6(R_{hb}/r_{jk})^{10}] \tag{2.102}$$

Note that for the hydrogen bond, the hydrogen atom *must* be the central atom. Several of these functions are identical to those appearing in the *intra*-molecular valenceangle descriptions above. There are significant differences in implementation however, arising from the fact that the three-body potentials are regarded as *inter*-molecular. Firstly, the atoms involved are defined by atom types, not specific indices. Secondly, there are *no* excluded atoms arising from the three body terms. (The inclusion of pair potentials may in fact be essential to maintain the structure of the system.)

The three body potentials are very short ranged, typically of order 3 Å. This property, plus the fact that three body potentials scale as N^3, where N is the number of particles, makes it essential that these terms are calculated by the link-cell method [29].

The calculation of the forces, virial and stress tensor as described in the section valence angle potentials above.

DL_POLY_2 applies no long range corrections to the three body potentials. The three body forces are calculated by the routine THBFRC.

2.3.4 Four Body Potentials

The four-body potentials in DL_POLY_2 are entirely inversion angle forms, primarily included to permit simulation of amorphous materials (particularly borate glasses). The potential forms available in DL_POLY_2 are as follows.

1. Harmonic: (**harm**)

$$U(\phi_{ijkn}) = \frac{1}{2}k(\phi_{ijkn} - \phi_0)^2 \tag{2.103}$$

2. Harmonic cosine: (**hcos**)

$$U(\phi_{ijkn}) = \frac{k}{2}(cos(\phi_{ijkn}) - cos(\phi_0))^2 \tag{2.104}$$

3. Planar potential: (**plan**)

$$U(\phi_{ijkn}) = A[1 - \cos(\phi_{ijkn})] \tag{2.105}$$

These functions are identical to those appearing in the *intra*-molecular inversion angle descriptions above. There are significant differences in implementation however, arising from the fact that the four-body potentials are regarded as *inter*-molecular. Firstly, the atoms involved are defined by atom types, not specific indices. Secondly, there are *no* excluded atoms arising from the four-body terms. (The inclusion of other potentials, for example pair potentials, may in fact be essential to maintain the structure of the system.)

The four body potentials are very short ranged, typically of order 3 Å. This property, plus the fact that four body potentials scale as N^4, where N is the number of particles, makes it essential that these terms are calculated by the link-cell method [29].

The calculation of the forces, virial and stress tensor described in the section on inversion angle potentials above.

DL_POLY_2 applies no long range corrections to the four body potentials. The four-body forces are calculated by the routine FBPFRC.

2.3.5 External Fields

In addition to the molecular force field, DL_POLY_2 allows the use of an *external* force field. Examples of field available include:

1. Electric field: (**elec**)

$$\underline{F_i} = \underline{F_i} + q_i.\underline{H} \tag{2.106}$$

2. Oscillating shear: (**oshm**)

$$\underline{F}_x = A\cos(2n\pi.z/L_z) \tag{2.107}$$

3. Continuous shear: (**shrx**)

$$\underline{v}_x = \frac{1}{2}A\frac{|z|}{z} \qquad : |z| > z_0 \tag{2.108}$$

4. Gravitational field: (**grav**)

$$\underline{F_i} = \underline{F_i} + m_i.\underline{H} \tag{2.109}$$

5. Magnetic field: (**magn**)

$$\underline{F_i} = \underline{F_i} + q_i.(\underline{v_i} \wedge \underline{H}) \tag{2.110}$$

6. Containing sphere: (**sphr**)

$$\underline{F} = A(R_0 - r)^{-n} \qquad : r > R_{cut} \tag{2.111}$$

It is recommended that the use of an external field should be accompanied by a thermostat (this does not apply to example 6, since this is a conservative field).

In DL_POLY_2 external field forces are handled by the routine EXTNFLD.

2.4 Long Ranged Electrostatic (Coulombic) Potentials

DL_POLY_2 incorporates several techniques for dealing with long ranged electrostatic potentials. [2] These are as follows.

1. Atomistic and charge group implementation.
2. Direct Coulomb sum;
3. Truncated and shifted Coulomb sum;
4. Coulomb sum with distance dependent dielectric;
5. Ewald sum;
6. Smooth Particle Mesh Ewald (SPME);
7. Reaction field;
8. Dynamical shell model.

Some of these techniques can be combined. For example 1, 3 and 4 can be used in conjunction with 7. The Ewald sum and SPME are restricted to periodic (or pseudo-periodic) systems only, though DL_POLY_2 can handle a broad selection of periodic boundary conditions, including cubic, orthorhombic, parallelepiped, truncated octahedral, hexagonal prism and rhombic dodecahedral. The Ewald sum is the method of choice for periodic systems. The other techniques can be used with either periodic or non-periodic systems, though in the case of the direct Coulomb sum, there are likely to be problems of convergence.

DL_POLY_2 will correctly handle the electrostatics of both molecular and atomic species. However it is assumed that the system is electrically neutral. A warning message is printed if the system is found to be charged, but otherwise the simulation proceeds as normal. No correction for non-neutrality is applied.

2.4.1 Atomistic and Charge Group Implementation

The Ewald sum is an accurate method for summing long-ranged potentials, such as the Coulomb potential, in periodic systems. This can be a very cpu intensive calculation and the use of more efficient, but less accurate methods, is common. Invariably this involves truncation of the potential at some finite distance $r_{\rm cut}$. If an atomistic scheme is used for the truncation criterion there is no guarantee that the interaction sphere will be neutral and spurious "charging" effects will almost certainly be seen in a simulation. This arises

[2] Unlike the other elements of the force field, the electrostatic forces are NOT specified in the input FIELD file, but by setting appropriate directives in the CONTROL file. See section 4.1.1.

because the potential being truncated is long-ranged ($1/r$ for charge-charge interactions). However if the cutoff scheme is based on *neutral* groups of atoms, then at worst, at long distance the interaction will be a dipole-dipole interaction and vary as $1/r^3$. The truncation effects at the cutoff are therefore much less severe than if an atomistic scheme is used. In DL_POLY_2 the interaction is evaluated between all atoms of both groups if any site of the first group is within the cutoff distance of any site of the second group. The groups are known interchangeably as "charge groups" or "neutral groups" in the documentation - which serves as a reminder that the advantages of using such a scheme are lost if the groups carry an overall charge. There is no formal requirement in DL_POLY_2 that the groups actually be electrically neutral.

The charge group scheme is more cpu intensive than a simple atomistic cutoff scheme as more computation is required to determine whether or not to include a set of interactions. However the size of the Verlet neighbourhood list (easily the largest array in DL_POLY_2) is considerably smaller with a charge group scheme than an atomistic scheme as only a list of interacting groups need be stored as opposed to a list of interacting atoms.

2.4.2 Direct Coulomb Sum

Use of the direct Coulomb sum is sometimes necessary for accurate simulation of isolated (nonperiodic) systems. It is *not* recommended for periodic systems.

The interaction potential for two charged ions is

$$U(r_{ij}) = \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}} \tag{2.112}$$

with q_ℓ the charge on an atom labelled ℓ, and r_{ij} the magnitude of the separation vector $\underline{r}_{ij} = \underline{r}_j - \underline{r}_i$.

The force on an atom j derived from this force is

$$\underline{f}_j = \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}^3}\underline{r}_{ij} \tag{2.113}$$

with the force on atom i the negative of this.

The contribution to the atomic virial is

$$\mathcal{W} = -\frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}} \tag{2.114}$$

which is simply the negative of the potential term.

The contribution to be added to the atomic stress tensor is

$$\sigma^{\alpha\beta} = r_{ij}^{\alpha} f_j^{\beta}, \tag{2.115}$$

where α, β are x, y, z components. The atomic stress tensor is symmetric.

In DL_POLY_2 these forces are handled by the routines COUL0 and COUL0NEU.

2.4.3 Truncated and Shifted Coulomb Sum

This form of the Coulomb sum has the advantage that it drastically reduces the range of electrostatic interactions, without giving rise to a violent step in the potential energy at the cutoff. Its main use is for preliminary preparation of systems and it is not recommended for realistic models.

The form of the potential function is

$$U(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0}\left\{\frac{1}{r_{ij}} - \frac{1}{r_{cut}}\right\} \tag{2.116}$$

with q_ℓ the charge on an atom labelled ℓ, r_{cut} the cutoff radius and r_{ij} the magnitude of the separation vector $\underline{r}_{ij} = \underline{r}_j - \underline{r}_i$.

The force on an atom j derived from this potential, within the radius r_{cut}, is

$$\underline{f}_j = \frac{1}{4\pi\epsilon_0}\frac{q_i q_j}{r_{ij}^3}\underline{r}_{ij} \tag{2.117}$$

with the force on atom i the negative of this.

The contribution to the atomic virial is

$$\mathcal{W} = -\underline{r}_{ij}\cdot\underline{f}_j \tag{2.118}$$

which is *not* the negative of the potential term in this case.

The contribution to be added to the atomic stress tensor is given by

$$\sigma^{\alpha\beta} = r_{ij}^{\alpha} f_j^{\beta}, \tag{2.119}$$

where α, β are x, y, z components. The atomic stress tensor is symmetric.

In DL_POLY_2 these forces are handled by the routine COUL1.

A further refinement of this approach is to truncate the $1/r$ potential at $r_{\rm cut}$ and add a linear term to the potential in order to make both the energy and the force zero at the cutoff. The potential is thus

$$U(r_{ij}) = \frac{q_i q_j}{4\pi\epsilon_0}\left[\frac{1}{r_{ij}} + \frac{r_{ij}}{r_{\rm cut}^2} - \frac{2}{r_{\rm cut}}\right] \tag{2.120}$$

with the force on atom j given by

$$\underline{f}_j = \frac{q_i q_j}{4\pi\epsilon_0}\left[\frac{1}{r_{ij}^2} - \frac{1}{r_{\rm cut}^2}\right]\underline{r}_{ij} \tag{2.121}$$

with the force on atom i the negative of this.

This removes the heating effects that arise from the discontinuity in the forces at the cutoff in the simple truncated and shifted potential. The physics of this potential however are little better. It is only recommended for very crude structure optimizations.

The contribution to the atomic virial is

$$\mathcal{W} = -\underline{r}_{ij} \cdot \underline{f}_j \tag{2.122}$$

which is *not* the negative of the potential term.

The contribution to be added to the atomic stress tensor is given by

$$\sigma^{\alpha\beta} = r_{ij}^{\alpha} f_j^{\beta}, \tag{2.123}$$

where α, β are x, y, z components. The atomic stress tensor is symmetric.

In DL_POLY_2 these forces are handled by the routine COUL4.

2.4.4 Coulomb Sum with Distance Dependent Dielectric

This potential attempts to address the difficulties of applying the direct Coulomb sum, without the brutal truncation of the previous case. It hinges on the assumption that the electrostatic forces are effectively 'screened' in real systems - an effect which is approximated by introducing a dielectic term that increases with distance.

The interatomic potential for two charged ions is

$$U(r_{ij}) = \frac{1}{4\pi\epsilon_0\epsilon(r_{ij})} \frac{q_i q_j}{r_{ij}} \tag{2.124}$$

with q_ℓ the charge on an atom labelled ℓ, and r_{ij} the magnitude of the separation vector $\underline{r}_{ij} = \underline{r}_j - \underline{r}_i$. $\epsilon(r)$ is the distance dependent dielectric function. In DL_POLY_2 it is assumed that this function has the form

$$\epsilon(r) = \epsilon r \tag{2.125}$$

where ϵ is a constant. Inclusion of this term effectively accelerates the rate of convergence of the Coulomb sum.

The force on an atom j derived from this potential is

$$\underline{f}_j = \frac{1}{2\pi\epsilon_0\epsilon} \frac{q_i q_j}{r_{ij}^4} \underline{r}_{ij} \tag{2.126}$$

with the force on atom i the negative of this.

The contribution to the atomic virial is

$$\mathcal{W} = -\underline{r}_{ij} \cdot \underline{f}_j \tag{2.127}$$

which is -2 times the potential term.

The contribution to be added to the atomic stress tensor is given by

$$\sigma^{\alpha\beta} = r_{ij}^{\alpha} f_j^{\beta}, \tag{2.128}$$

where α, β are x, y, z components. The atomic stress tensor is symmetric.

In DL_POLY_2 these forces are handled by the routines COUL2 and COUL2NEU.

2.4.5 Ewald Sum

The Ewald sum [10] is the best technique for calculating electrostatic interactions in a periodic (or pseudo-periodic) system.

The basic model for a neutral periodic system is a system of charged point ions mutually interacting via the Coulomb potential. The Ewald method makes two amendments to this simple model. Firstly each ion is effectively neutralised (at long range) by the superposition of a spherical gaussian cloud of opposite charge centred on the ion. The combined assembly of point ions and gaussian charges becomes the *Real Space* part of the Ewald sum, which is now short ranged and treatable by the methods described above (section 2.1). [3] The second modification is to superimpose a second set of gaussian charges, this time with the same charges as the original point ions and again centred on the point ions (so nullifying the effect of the first set of gaussians). The potential due to these gaussians is obtained from Poisson's equation and is solved as a Fourier series in *Reciprocal Space*. The complete Ewald sum requires an additional correction, known as the self energy correction, which arises from a gaussian acting on its own site, and is constant. Ewald's method therefore replaces a potentially infinite sum in real space by two finite sums: one in real space and one in reciprocal space; and the self energy correction.

For molecular systems, as opposed to systems comprised simply of point ions, additional modifications are necessary to correct for the excluded (intra-molecular) Coulombic interactions. In the real space sum these are simply omitted. In reciprocal space however, the effects of individual gaussian charges cannot easily be extracted, and the correction is made in real space. It amounts to removing terms corresponding to the potential energy of an ion ℓ due to the gaussian charge on a neighbouring charge m (or *vice versa*). This correction appears as the final term in the full Ewald formula below. The distinction between the error function erf and the more usual complementary error function $erfc$ found in the real space sum, should be noted.

The total electrostatic energy is given by the following formula.

$$U_c = \frac{1}{2V_o\epsilon_0}\sum_{\underline{k}\neq\underline{0}}^{\infty}\frac{\exp(-k^2/4\alpha^2)}{k^2}\left|\sum_j^N q_j\exp(-i\underline{k}\cdot\underline{r}_j)\right|^2 + \frac{1}{4\pi\epsilon_0}\sum_{n<j}^{N^*}\frac{q_jq_n}{r_{nj}}erfc(\alpha r_{nj}) - \frac{1}{4\pi\epsilon_0}\sum_{molecules}\sum_{\ell\leq m}^{M^*} q_\ell q_m\left\{\delta_{\ell m}\frac{\alpha}{\sqrt{\pi}} + \frac{erf(\alpha r_{\ell m})}{r_{\ell m}^{1-\delta_{\ell m}}}\right\}, \quad (2.129)$$

where N is the number of ions in the system and N^* the same number discounting any excluded (intramolecular) interactions. M^* represents the number of excluded atoms in a given molecule and includes the atomic self correction. V_o is the simulation cell volume and $\underline{k}$ is a reciprocal lattice vector defined by

$$\underline{k} = \ell\underline{u} + m\underline{v} + n\underline{w} \quad (2.130)$$

[3] Strictly speaking, the real space sum ranges over all periodic images of the simulation cell, but in the DL_POLY_2 implementation, the parameters are chosen to restrict the sum to the simulation cell and its nearest neighbours i.e. the *minimum images* of the cell contents.

where ℓ, m, n are integers and $\underline{u}, \underline{v}, \underline{w}$ are the *reciprocal space* basis vectors. Both V_o and $\underline{u}, \underline{v}, \underline{w}$ are derived from the vectors $(\underline{a}, \underline{b}, \underline{c})$ defining the simulation cell. Thus

$$V_o = |\underline{a} \cdot \underline{b} \times \underline{c}| \tag{2.131}$$

and

$$\begin{aligned} \underline{u} &= 2\pi \frac{\underline{b} \times \underline{c}}{\underline{a} \cdot \underline{b} \times \underline{c}} \\ \underline{v} &= 2\pi \frac{\underline{c} \times \underline{a}}{\underline{a} \cdot \underline{b} \times \underline{c}} \\ \underline{w} &= 2\pi \frac{\underline{a} \times \underline{b}}{\underline{a} \cdot \underline{b} \times \underline{c}}. \end{aligned} \tag{2.132}$$

With these definitions, the Ewald formula above is applicable to general periodic systems. (A small additional modification is necessary for rhombic dodecahedral and truncated octahedral simulation cells [30].)

In practice the convergence of the Ewald sum is controlled by three variables: the real space cutoff r_{cut}; the convergence parameter α and the largest reciprocal space vector $\underline{k}_{max}$ used in the reciprocal space sum. These are discussed more fully in section 3.3.5. DL_POLY_2 can provide estimates if requested (see CONTROL file description 4.1.1.

The force on an atom j is obtained by differentiation and is

$$\begin{aligned} \underline{f}_j = & -\frac{q_j}{V_o \epsilon_0} \sum_{\underline{k} \neq \underline{0}}^{\infty} i\underline{k} \exp(\underline{k} \cdot \underline{r}_j) \frac{\exp(-k^2/4\alpha^2)}{k^2} \sum_n^N q_n \exp(-i\underline{k} \cdot \underline{r}_n) \\ & + \frac{q_j}{4\pi\epsilon_0} \sum_n^{N^*} \frac{q_n}{r_{nj}^3} \left\{ erfc(\alpha r_{nj}) + \frac{2\alpha r_{nj}}{\sqrt{\pi}} \exp(-\alpha^2 r_{nj}^2) \right\} \underline{r}_{nj} \\ & - \frac{q_j}{4\pi\epsilon_0} \sum_\ell^{M^*} \frac{q_\ell}{r_{\ell j}^3} \left\{ erf(\alpha r_{\ell j}) - \frac{2\alpha r_{\ell j}}{\sqrt{\pi}} \exp(-\alpha^2 r_{\ell j}^2) \right\} \underline{r}_{\ell j} \end{aligned} \tag{2.133}$$

The electrostatic contribution to the system virial can be obtained as the negative of the Coulombic energy. However in DL_POLY_2 this formal equality can be used as a check on the convergence of the Ewald sum. The actual electrostatic virial is obtained during the calculation of the diagonal of the stress tensor.

The electrostatic contribution to the stress tensor is given by

$$\begin{aligned} \underline{\underline{\sigma}} = & \frac{1}{2V_o\epsilon_0} \sum_{\underline{k} \neq \underline{0}}^{\infty} \left\{ \underline{\underline{1}} - 2\left(\frac{1}{4\alpha^2} + \frac{1}{k^2}\right) \underline{\underline{\mathbf{K}}} \right\} \frac{\exp(-k^2/4\alpha^2)}{k^2} |\sum_j^N q_j \exp(-i\underline{k} \cdot \underline{r}_j)|^2 \\ & + \frac{1}{4\pi\epsilon_0} \sum_{j<n}^{N^*} \frac{q_j q_n}{r_{nj}^3} \left\{ erfc(\alpha r_{nj}) + \frac{2\alpha r_{nj}}{\sqrt{\pi}} \exp(-\alpha^2 r_{nj}^2) \right\} \underline{\underline{\mathbf{R_{nj}}}} \\ & - 4\pi\epsilon_0 \sum_{j<\ell}^{M^*} \frac{q_j q_\ell}{r_{\ell j}^3} \left\{ erf(\alpha r_{\ell j}) - \frac{2\alpha r_{\ell j}}{\sqrt{\pi}} \exp(-\alpha^2 r_{\ell j}^2) \right\} \underline{\underline{\mathbf{R_{\ell j}}}}, \end{aligned} \tag{2.134}$$

where matrices $\underline{\underline{\mathbf{K}}}$ and $\underline{\underline{\mathbf{R}_{\ell j}}}$ are defined as follows.

$$K^{\alpha\beta} = k^{\alpha}k^{\beta} \tag{2.135}$$
$$R_{\ell j}^{\alpha\beta} = r_{\ell j}^{\alpha}r_{\ell j}^{\beta} \tag{2.136}$$

In DL_POLY_2 the full Ewald sum is handled by several routines: EWALD1 and EWALD1A handle the reciprocal space terms; EWALD2, EWALD2_2PT, EWALD2_RSQ and EWALD4, EWALD4_2PT handle the real space terms (with the same Verlet neighbour list routines that are used to calculate the short range forces); and EWALD3 calculates the self interaction corrections. It should be noted that the Ewald potential and force interpolation arrays in DL_POLY_2 are `erc` and `fer` respectively.

2.4.6 Smooth Particle Mesh Ewald

As its name implies the Smooth Particle Mesh Ewald (SPME) method is a modification of the standard Ewald method. DL_POLY_2 implements the SPME method of Essmann *et al.* [31]. Formally this method is capable of treating van der Waals forces also, but in DL_POLY_2 it is confined to electrostatic forces only. The main difference from the standard Ewald method is in its treatment of the the reciprocal space terms. By means of an interpolation procedure involving (complex) B-splines, the sum in reciprocal space is represented on a three dimensional rectangular grid. In this form the Fast Fourier Transform (FFT) may be used to perform the primary mathematical operation, which is a 3D convolution. The efficiency of these procedures greatly reduces the cost of the reciprocal space sum when the range of $\underline{k}$ vectors is large. The method (briefly) is as follows (for full details see [31]):

1. Interpolation of the $exp(-i\underline{k}\cdot\underline{r}_j)$ terms (given here for one dimension):

$$exp(2\pi i u_j k/L) \approx b(k)\sum_{\ell=-\infty}^{\infty} M_n(u_j-\ell)exp(2\pi ik\ell/K) \tag{2.137}$$

   in which k is the integer index of the $\underline{k}$ vector in a principal direction, K is the total number of grid points in the same direction and u_j is the fractional coordinate of ion j scaled by a factor K (i.e. $u_j = Ks_j^x$). Note that the definition of the B-splines implies a dependence on the integer K, which limits the formally infinite sum over ℓ. The coefficients $M_n(u)$ are B-splines of order n and the factor $b(k)$ is a constant computable from the formula:

$$b(k) = exp(2\pi i(n-1)k/K)\left[\sum_{\ell=0}^{n-2} M_n(\ell+1)exp(2\pi ik\ell/K)\right]^{-1} \tag{2.138}$$

2. Approximation of the structure factor $S(\underline{k})$:

$$S(\underline{k}) \approx b_1(k_1)b_2(k_2)b_3(k_3)Q^{\dagger}(k_1,k_2,k_3) \tag{2.139}$$

where $Q^\dagger(k_1,k_2,k_3)$ is the discrete Fourier transform of the *charge array* $Q(\ell_1,\ell_2,\ell_3)$ defined as

$$Q(\ell_1,\ell_2,\ell_3) = \sum_{j=1}^{N} q_j \sum_{n_1,n_2,n_3} M_n(u_{1j}-\ell_1-n_1L_1)M_n(u_{2j}-\ell_2-n_2L_2)M_n(u_{3j}-\ell_3-n_3L_3) \tag{2.140}$$

(in which the sums over $n_{1,2,3}$ etc are required to capture contributions from all relevant periodic cell images, which in practice means the nearest images.)

3. Approximating the reciprocal space energy U_{recip}:

$$U_{recip} = \frac{1}{2V_o\epsilon_0} \sum_{k_1,k_2,k_3} G^\dagger(k_1,k_2,k_3)Q(k_1,k_2,k_3) \tag{2.141}$$

in which $G^\dagger$ is the discrete Fourier transform of the function

$$G(k_1,k_2,k_3) = \frac{\exp(-k^2/4\alpha^2)}{k^2} B(k_1,k_2,k_3)(Q^\dagger(k_1,k_2,k_3))^* \tag{2.142}$$

and where

$$B(k_1,k_2,k_3) = |b_1(k_1)|^2|b_2(k_2)|^2|b_3(k_3)|^2 \tag{2.143}$$

and $(Q^\dagger(k_1,k_2,k_3))^*$ is the complex conjgate of $Q^\dagger(k_1,k_2,k_3)$. The function $G(k_1,k_2,k_3)$ is thus a relatively simple product of the gaussian screening term appearing in the conventional Ewald sum, the function $B(k_1,k_2,k_3)$ and the discrete Fourier transform of $Q(k_1,k_2,k_3)$

4. Calculating the atomic forces, which are given formally by:

$$f_j^\alpha = -\frac{\partial U_{recip}}{\partial r_j^\alpha} = -\frac{1}{V_o\epsilon_0} \sum_{k_1,k_2,k_3} G^\dagger(k_1,k_2,k_3) \frac{\partial Q(k_1,k_2,k_3)}{\partial r_j^\alpha} \tag{2.144}$$

Fortunately, due to the recursive properties of the B-splines, these formulae are easily evaluated.

The virial and the stres tensor are calculated in the same manner as for the conventional Ewald sum.

2.4.7 Reaction Field

In the reaction field method it is assumed that any given molecule is surrounded by a spherical cavity of finite radius within which the electrostatic interactions are calculated explicitly. Outside the cavity the system is treated as a dielectric continuum. The occurence of any net dipole within the cavity induces a polarisation in the dielectric, which in turn interacts with the given molecule. The model allows the replacement of the infinite Coulomb sum by a finite sum plus the reaction field.

The reaction field model coded into DL_POLY_2 is the implementation of Neumann based on charge-charge interactions [32]. In this model, the total Coulombic potential is given by

$$U_c = \frac{1}{4\pi\epsilon_0} \sum_{j<n} q_j q_n \left[\frac{1}{r_{nj}} + \frac{B_0 r_{nj}^2}{2R_c^3} \right] \tag{2.145}$$

where the second term on the right is the reaction field correction to the explicit sum, with R_c the radius of the cavity. The constant B_0 is defined as

$$B_0 = \frac{2(\epsilon_1 - 1)}{(2\epsilon_1 + 1)}, \tag{2.146}$$

with ϵ_1 the dielectric constant outside the cavity. The effective pair potential is therefore

$$U(r_{nj}) = \frac{1}{4\pi\epsilon_0} q_j q_n \left[\frac{1}{r_{nj}} + \frac{B_0 r_{nj}^2}{2R_c^3} \right]. \tag{2.147}$$

This expression unfortunately leads to large fluctuations in the system Coulombic energy, due to the large 'step' in the function at the cavity boundary. In DL_POLY_2 this is countered by subtracting the value of the potential at the cavity boundary from each pair contribution. The term subtracted is

$$\frac{1}{4\pi\epsilon_0} \frac{q_j q_n}{R_c} \left[1 + \frac{B_0}{2} \right]. \tag{2.148}$$

The effective pair force on an atom j arising from another atom n within the cavity is given by

$$\underline{f}_j = \frac{q_j q_n}{4\pi\epsilon_0} \left[\frac{1}{r_{nj}^3} - \frac{B_0}{R_c^3} \right] \underline{r}_{nj}. \tag{2.149}$$

The contribution of each effective pair interaction to the atomic virial is

$$\mathcal{W} = -\underline{r}_{nj} \cdot \underline{f}_j \tag{2.150}$$

and the contribution to the atomic stress tensor is

$$\sigma^{\alpha\beta} = r_{nj}^{\alpha} f_j^{\beta}. \tag{2.151}$$

In DL_POLY_2 the reaction field is handled by the routines COUL3 and COUL3NEU.

2.4.8 Dynamical Shell Model

An atom or ion is polarisable if it develops a dipole moment when placed in an electric field. It is commonly expressed by the equation

$$\underline{\mu} = \alpha \underline{E}, \tag{2.152}$$

where $\underline{\mu}$ is the induced dipole and $\underline{E}$ is the electric field. The constant α is the polarisability.

The dynamical shell model is a method of incorporating polarisability into a molecular dynamics simulation. The method used in DL_POLY_2 is that devised by Fincham *et al* [33] and is known as the adiabatic shell model. An alternative model is presented in [34].

In the *static* shell model a polarisable atom is represented by a massive core and massless shell, connected by a harmonic spring, hereafter called the core-shell unit. The core and shell carry different electric charges, the sum of which equals the charge on the original atom. There is no electrostatic interaction (i.e. self interaction) between the core and shell of the same atom. Non-Coulombic interactions arise from the shell alone. The effect of an electric field is to separate the core and shell, giving rise to a *polarisation* dipole. The condition of static equilibrium gives the polarisability as:

$$\alpha = (2q_s^2 - q_c^2)/k \tag{2.153}$$

where q_s and q_c are the shell and core charges and k is the force constant of the harmonic spring.

In the adiabatic method, a fraction of the atomic mass is assigned to the shell to permit a dynamical description. The fraction of mass is chosen to ensure that the natural frequency of vibration ν of the harmonic spring (i.e.

$$\nu = \frac{1}{2\pi}\left[\frac{k}{x(1-x)m}\right]^{1/2}, \tag{2.154}$$

with m the atomic mass,) is well above the frequency of vibration of the whole atom in the bulk system. Dynamically the core-shell unit resembles a diatomic molecule with a harmonic bond, however the high vibrational frequency of the bond prevents effective exchange of kinetic energy between the core-shell unit and the remaining system. Therefore, from an initial condition in which the core-shell units have negligible internal vibrational energy, the units will remain close to this condition throughout the simulation. This is essential if the core shell unit is to maintain a net polarisation. (In practice there is a slow leakage of kinetic energy into the core-shell units, but this should should not amount to more than a few percent of the total kinetic energy.)

The calculation of the virial and stress tensor in this model is based on that for a diatomic molecule with charged atoms. The electrostatic and short ranged forces are calculated as described above. The forces of the harmonic springs are calculated as described for intramolecular harmonic bonds. The relationship between the kinetic energy and the temperature is different however, as the core-shell unit is permitted only three translational degrees of freedom, and the degrees of freedom corresponding to rotation and vibration of the unit are discounted (the kinetic energy of these is regarded as zero).

In DL_POLY_2 the shell forces are handled by the routine SHLFRC. The kinetic energy is calculated by CORSHL and the routine SHQNCH performs the temperature scaling. The dynamical shell model is used in conjunction with the methods for long range forces described above.

2.5 Integration algorithms

DL_POLY integration algorithms are based around the Verlet leapfrog scheme, which is both simplectic (time reversible) and simple in nature [10]. It generates trajectories in the microcanonical (NVE) ensemble in which the total energy (kinetic plus potential energy) is conserved. If this property drifts or fluctuates significantly in the course of a simulation it indicates that the timestep is too large or the potential cutoffs too small (relative r.m.s. fluctuations in the total energy of 10^{-5} are typical with this algorithm).

The algorithm requires values of position ($\underline{r}$) and force ($\underline{f}$) at time t while the velocities ($\underline{v}$) are half a timestep behind. The first step is to advance the velocities to $t + (1/2)\Delta t$ by integration of the force:

$$\underline{v}(t + \frac{1}{2}\Delta t) \leftarrow \underline{v}(t - \frac{1}{2}\Delta t) + \Delta t \, \frac{\underline{f}(t)}{m} \tag{2.155}$$

where m is the mass of a site and Δt is the timestep.

The positions are then advanced using the new velocities:

$$\underline{r}(t + \Delta t) \leftarrow \underline{r}(t) + \Delta t \, \underline{v}(t + \frac{1}{2}\Delta t) \tag{2.156}$$

Molecular dynamics simulations normally require properties that depend on position and velocity *at the same time* (such as the sum of potential and kinetic energy). The velocity at time t is obtained from the average of the velocities half a timestep either side of time t:

$$\underline{v}(t) = \frac{1}{2}\left[\underline{v}(t - \frac{1}{2}\Delta t) + \underline{v}(t + \frac{1}{2}\Delta t)\right] \tag{2.157}$$

The instantaneous temperature, for example can then be obtained from the atomic velocities assuming the system has no net momentum:

$$\mathcal{T} = \frac{\sum_{i=1}^{\mathcal{N}} m_i v_i^2(t)}{k_B f} \tag{2.158}$$

where i labels particles (which can be atoms or rigid molecules), $\mathcal{N}$ the number of particles in the system, k_B Boltzmanns constant and f the number of degrees of freedom in the system ($3\mathcal{N} - 3$ if the system is periodic and without constraints).

The routine NVE_0 implements the Verlet leapfrog algorithm and calculates the instantaneous temperature. The conserved quantity is the total energy of the system

$$\mathcal{H}_{\rm NVE} = U + KE \tag{2.159}$$

where U is the potential energy of the system and KE the kinetic energy at time t.

The full selection of integrration algorithms within DL_POLY_2 is as follows:

NVE_0	Verlet leapfrog
NVE_1	Verlet leaprog with RD-SHAKE

NVEQ_1 Rigid units with FIQA and RD-SHAKE
NVEQ_2 Linked rigid units with QSHAKE
NVT_B0 Constant T (Berendsen [14]) with Verlet leapfrog
NVT_B1 Constant T (Berendsen [14]) with RD-SHAKE
NVT_E0 Constant T (Evans [15]) with Verlet leapfrog
NVT_E1 Constant T (Evans [15]) with RD-SHAKE
NVT_H0 Constant T (Hoover [16]) with Verlet leapfrog
NVT_H1 Constant T (Hoover [16]) with RD-SHAKE
NVTQ_B1 Constant T (Berendsen [14]) with FIQA and RD-SHAKE
NVTQ_B2 Constant T (Berendsen [14]) with QSHAKE
NVTQ_H1 Constant T (Hoover [16]) with FIQA and RD-SHAKE
NVTQ_H2 Constant T (Hoover [16]) with QSHAKE
NPT_B0 Constant T,P (Berendsen [14]) with Verlet leapfrog
NPT_B1 Constant T,P (Berendsen [14]) with FIQA and RD-SHAKE
NPT_B3 Constant T,$\underline{\underline{\sigma}}$ (Berendsen [14]) with RD-SHAKE
NPT_H0 Constant T,P+ (Hoover [16]) with Verlet leapfrog
NPT_H1 Constant T,P+ (Hoover [16]) with RD-SHAKE
NPT_H3 Constant T,$\underline{\underline{\sigma}}$ (Hoover [16]) with RD-SHAKE
NPTQ_B1 Constant T,P (Berendsen [14]) with FIQA and RD-SHAKE
NPTQ_B2 Constant T,P (Berendsen [14]) with QSHAKE
NST_B0 Constant T,$\underline{\underline{\sigma}}$ (Berendsen [14]) with Verlet leapfrog
NST_H0 Constant T,$\underline{\underline{\sigma}}$ (Hoover [16]) with Verlet leapfrog
NPTQ_B3 Constant T,$\underline{\underline{\sigma}}$ (Berendsen [14]) with FIQA and RD-SHAKE
NPTQ_B4 Constant T,$\underline{\underline{\sigma}}$ (Berendsen [14]) with QSHAKE
NPTQ_H1 Constant T,P (Hoover [16]) with FIQA and RD-SHAKE
NPTQ_H2 Constant T,P (Hoover [16]) with QSHAKE
NPTQ_H3 Constant T,$\underline{\underline{\sigma}}$ (Hoover [16]) with FIQA and RD-SHAKE
NPTQ_H4 Constant T,$\underline{\underline{\sigma}}$ (Hoover [16]) with QSHAKE

In the above table the FIQA algorithm is Fincham's Implicit Quaternion Algorithm [12] and QSHAKE is the DL_POLY_2 algorithm combining rigid bonds and rigid bodies in the same molecule [13].

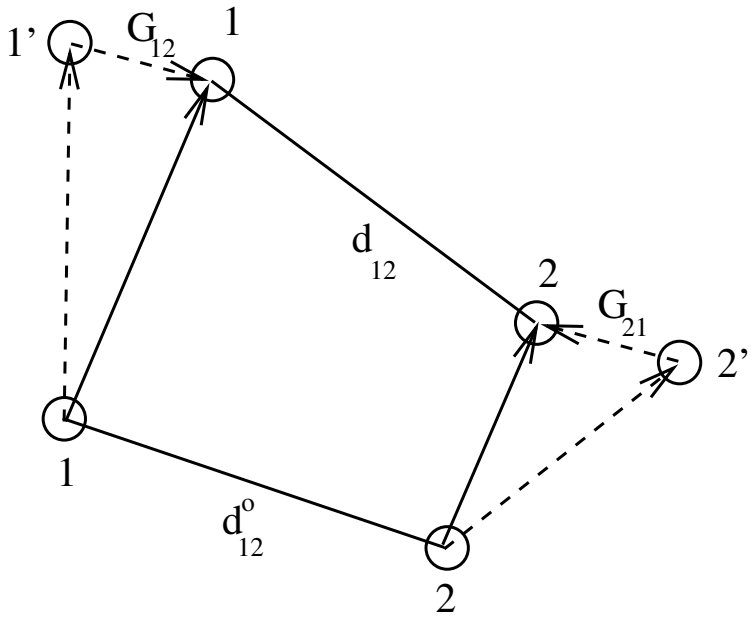
2.5.1 Bond Constraints

The SHAKE algorithm for bond constraints was devised by Ryckaert *et al.* [11] and is widely used in molecular simulation. It is a two stage algorithm based on the Verlet integration scheme [10]. DL_POLY_2 employs a leapfrog variant. In the first stage the Verlet leapfrog algorithm calculates the motion of the atoms in the system assuming a complete absence of the rigid bond forces. The positions of the atoms at the end of this stage do not conserve the distance constraint required by the rigid bond and a correction is necessary. In the second stage the deviation in the length of a given rigid bond is used retrospectively to compute the constraint force needed to conserve the bondlength. It is relatively simple to

show that the constraint force has the form

$$\underline{G}_{ij} \approx \frac{\mu_{ij}(d_{ij}^2 - d_{ij}'^2)}{2\Delta t^2 \underline{d}_{ij}^o \cdot \underline{d}_{ij}'} \underline{d}_{ij}^o \tag{2.160}$$

where: μ_{ij} is the reduced mass of the two atoms connected by the bond; $\underline{d}_{ij}^o$ and $\underline{d}_{ij}'$ are the original and intermediate bond vectors; d_{ij} is the constrained bondlength; and Δt is the Verlet integration time step. It should be noted that this formula is an approximation only.



The SHAKE algorithm calculates the constraint force $\underline{G}_{12} = -\underline{G}_{21}$ that conserves the bondlength d_{12} between atoms 1 and 2, following the initial movement to positions $1'$ and $2'$ under the unconstrained forces $\underline{F}_1$ and $\underline{F}_2$.

For a system of simple diatomic molecules, computation of the constraint force will, in principle, allow the correct atomic positions to be calculated in one pass. However in the general polyatomic case this correction is merely an interim adjustment, not only because the above formula is approximate, but the successive correction of other bonds in a molecule has the effect of perturbing previously corrected bonds. The SHAKE algorithm is therfore iterative, with the correction cycle being repeated for all bonds until each has converged to the correct length, within a given tolerance. The tolerance may be of the order 10^{-4} Åto 10^{-8} Ådepending on the precision desired.

The procedure may be summarised as follows:

1. All atoms in the system are moved using the Verlet algorithm, assuming an absence of rigid bonds (constraint forces). (This is stage 1 of the SHAKE algorithm.)

2. The deviation in each bondlength is used to calculate the corresponding constraint force (2.160) that (retrospectively) 'corrects' the bond length.

3. After the correction (2.160) has been applied to all bonds, every bondlength is checked. If the largest deviation found exceeds the desired tolerance, the correction calculation is repeated.

4. Steps 2 and 3 are repeated until all bondlengths satisfy the convergence criterion (This iteration constitutes stage 2 of the SHAKE algorithm).

The parallel version of this algorithm, as implemented in DL_POLY_2 , is known as RD_SHAKE [9] (see section 2.6.8). The subroutine NVE_1 implements the Verlet leapfrog algorithm with bond constraints. The routine RDSHAKE_1 is called to apply the SHAKE corrections to position.

It should be noted that the fully converged constraint forces G_{ij} make a contribution to the system virial and the stress tensor.

The contribution to be added to the atomic virial (for each constrained bond) is

$$\mathcal{W} = -\underline{d}_{ij} \cdot \underline{G}_{ij}. \tag{2.161}$$

The contribution to be added to the atomic stress tensor is given by

$$\sigma^{\alpha\beta} = d_{ij}^{\alpha} G_{ij}^{\beta}, \tag{2.162}$$

where α and β indicate the x, y, z components. The atomic stress tensor derived from the pair forces is symmetric.

2.5.2 Potential of Mean Force (PMF) Constraints and the Evaluation of Free Energy

A generalization of bond constraints can be made to constrain a system to some point along a reaction coordinate. A simple example of such a reaction coordinate would be the distance between two ions in solution. If a number of simulations are conducted with the system constrained to different points along the reaction coordinate then the mean constraint force may be plotted as a function of reaction coordinate and the function integrated to obtain the free energy for the overall process [35]. The PMF constraint force, virial and contributions to the stress tensor are obtained in a manner analagous to that for a bond constraint (see previous section). The only difference is that the constraint is now applied between the centres of two groups which need not be atoms alone. DL_POLY_2 reports the PMF constraint virial, $\mathcal{W}$, for each simulation. Users can convert this to the PMF constraint force from

$$G_{\rm PMF} = -\mathcal{W}_{\rm PMF}/d_{\rm PMF}$$

where $d_{\rm PMF}$ is the constraint distance between the two groups used to define the reaction coordinate.

2.5.3 Thermostats

The system may be coupled to a heat bath to ensure that the average system temperature is maintained close to the requested temperature, $T_{\rm ext}$. When this is done the equations of motion are modified and the system no longer samples the microcanonical ensemble. Instead trajectories in the canonical (NVT) ensemble, or something close to it are generated. DL_POLY_2 comes with three different thermostats: Nosé-Hoover [16], Berendsen [14], and Gaussian constraints [15]. Of these only the Nosé-Hoover algorithm generates trajectories in the canonical (NVT) ensemble. The other methods will produce properties that typically differ from canonical averages by $\mathcal{O}(1/\mathcal{N})$ [10]

2.5.3.1 Nosé- Hoover Thermostat

In the Nosé-Hoover algorithm [16] Newton's equations of motion are modified to read:

$$\begin{aligned} \frac{d\underline{r}(t)}{dt} &= \underline{v}(t) \\ \frac{d\underline{v}(t)}{dt} &= \frac{\underline{\underline{f}}(t)}{m} - \chi(t)\underline{v}(t) \end{aligned} \tag{2.163}$$

(2.164)

The friction coefficient, χ, is controlled by the first order differential equation

$$\frac{d\chi(t)}{dt} = \frac{1}{\tau_T^2}\left(\frac{\mathcal{T}}{T_{\rm ext}} - 1\right) \tag{2.165}$$

where τ_T is a specified time constant (normally in the range [0.5, 2] ps). In DL_POLY_2 χ is stored at half timesteps as it has dimensions of (1/time). The integration takes place as:

$$\begin{aligned} \chi(t+\frac{1}{2}\Delta t) &\leftarrow \chi(t-\frac{1}{2}\Delta t) + \frac{\Delta t}{\tau_T^2}\left(\frac{\mathcal{T}}{T_{\rm ext}} - 1\right) \\ \chi(t) &\leftarrow \frac{1}{2}\left[\chi(t-\frac{1}{2}\Delta t) + \chi(t+\frac{1}{2}\Delta t)\right] \\ \underline{v}(t+\frac{1}{2}\Delta t) &\leftarrow \underline{v}(t-\frac{1}{2}\Delta t) + \Delta t\left[\frac{\underline{\underline{f}}(t)}{m} - \chi(t)\underline{v}(t)\right] \\ \underline{v}(t) &\leftarrow \frac{1}{2}\left[\underline{v}(t-\frac{1}{2}\Delta t) + \underline{v}(t+\frac{1}{2}\Delta t)\right] \\ \underline{r}(t+\Delta t) &\leftarrow \underline{r}(t) + \Delta t\,\underline{v}(t+\frac{1}{2}\Delta t) \end{aligned} \tag{2.166}$$

Since $\underline{v}(t)$ is required to calculate $\mathcal{T}$ and itself, the algorithm requires several iterations to obtain self consistency. In DL_POLY_2 the number of iterations is set to 3 (4 if the system has bond constraints). The iteration procedure is started with the standard Verlet leapfrog prediction of $\underline{v}(t)$ and $\mathcal{T}$. The conserved quantity is derived from the extended Hamiltonian

for the system which, to within a constant, is the Helmholtz free energy:

$$\mathcal{H}_{\rm NVT} = \mathcal{H}_{\rm NVE} + f k_B T_{\rm ext} \left(\frac{\tau_T^2 \chi^2(t)}{2} + \int_o^t \chi(s) ds \right) \tag{2.167}$$

If bond constraints are present an extra iteration is required due to the call to the SHAKE routine. Note that the SHAKE corrections need only be applied during the first iteration as subsequent to this the velocities, relative to the bond c.o.m. velocity, will be orthogonal to the bond vectors. The velocity scaling imposed by the thermostat is isotropic so does not destroy this orthogonality. The algorithm is implemented in the DL_POLY routines NVT_H0 and NVT_H1, the latter being for systems with bond constraints.

2.5.3.2 Berendsen Thermostat

In the Berendsen algorithm the instantaneous temperature is pushed towards the desired temperature by scaling the velocities at each step:

$$\begin{aligned}
\chi &\leftarrow \left[1 + \frac{\Delta t}{\tau_T} \left(\frac{T_{\rm ext}}{\mathcal{T}} - 1 \right) \right]^{1/2} \\
\underline{v}(t + \frac{1}{2}\Delta t) &\leftarrow \left[\underline{v}(t - \frac{1}{2}\Delta t) + \Delta t \frac{\underline{f}(t)}{m} \right] \chi \\
\underline{v}(t) &\leftarrow \frac{1}{2} \left[\underline{v}(t - \frac{1}{2}\Delta t) + \underline{v}(t + \frac{1}{2}\Delta t) \right] \\
\underline{r}(t + \Delta t) &\leftarrow \underline{r}(t) + \Delta t \, \underline{v}(t + \frac{1}{2}\Delta t)
\end{aligned} \tag{2.168}$$

As with the Nosé-Hoover thermostat iteration is required to obtain self consistency of χ, $\underline{v}(t)$ and $\mathcal{T}$, although it should be noted χ has different roles in the two thermostats. The Berendsen algorithm conserves total momentum but not energy.

As with the Nosé-Hoover algorithm the presence of constraint bonds requires an additional iteration with one application of SHAKE corrections. The algorithm is implemented in the DL_POLY routines NVT_B0 and NVT_B1, the latter being for systems with bond constraints.

2.5.4 Gaussian Constraints

Kinetic temperature can be made a constant of the equations of motion by imposing an additional constraint on the system. If one writes the equations of motions as :

$$\frac{d\underline{r}(t)}{dt} = \underline{v}(t) \tag{2.169}$$

$$\frac{d\underline{v}(t)}{dt} = \frac{\underline{f}(t)}{m} - \chi(t)\underline{v}(t) \tag{2.170}$$

with the temperature constraint

$$\frac{d\mathcal{T}}{dt} \propto \frac{d}{dt}\left(\sum_i (m_i v_i)^2\right) \propto \sum_i m_i^2 \underline{v}_i(t) \cdot \underline{f}_i(t) = 0 \tag{2.171}$$

then choosing

$$\chi = \frac{\sum_i m_i \underline{v}_i(t).\underline{f}_i(t)}{\sum_i m_i^2 v_i^2(t)} \tag{2.172}$$

minimizes the "least squares" differences between the Newtonian and constrained trajectories. Following Brown and Clarke [36] the algorithm is implemented by calculating $\eta = 1/(1 + \chi\Delta t/2)$

$$\begin{aligned} \eta &\leftarrow \sqrt{\frac{T_{\rm ext}}{\mathcal{T}}} \\ \underline{v}(t+\frac{1}{2}\Delta t) &\leftarrow (2\eta - 1)\underline{v}(t-\frac{1}{2}\Delta t) + \eta\Delta t\frac{\underline{f}(t)}{m} \\ \underline{r}(t+\Delta t) &\leftarrow \underline{r}(t) + \Delta t\, \underline{v}(t+\frac{1}{2}\Delta t) \end{aligned} \tag{2.173}$$

where $\mathcal{T}$ is obtained from standard Verlet leapfrog integration. Only one iteration is needed (two if the system has bond constraints) to constrain the instantaneous temperature to exactly $T_{\rm ext}$ however energy is not conserved by this algorithm.

The algorithm is implemented in the DL_POLY routines NVT_E0 and NVT_E1. The latter is for systems with bond constraints.

2.5.5 Barostats

The size and shape of the simulation cell may be dynamically adjusted by coupling the system to a barostat in order to obtain a desired average pressure ($P_{\rm ext}$) and/or isotropic stress tensor ($\underline{\underline{\sigma}}$). DL_POLY_2 has two such algorithms: a Hoover type barostat and the Berendsen barostat. Only the former has a well defined conserved quantity.

2.5.5.1 The Hoover Barostat

DL_POLY_2 uses the Melchionna modification of the Hoover algorithm [37] in which the equations of motion involve a Nosé - Hoover thermostat and a barostat in the same spirit.

Cell size variation

For isotropic fluctuations the equations of motion are:

$$\begin{aligned} \frac{d\underline{r}(t)}{dt} &= \underline{v}(t) + \eta(\underline{r}(t) - \underline{R}_0) \\ \frac{d\underline{v}(t)}{dt} &= \frac{\underline{\underline{f}}(t)}{m} - [\chi(t) + \eta(t)]\,\underline{v}(t) \end{aligned}$$

$$\begin{aligned}
\frac{d\chi(t)}{dt} &= \frac{1}{\tau_T^2}\left(\frac{\mathcal{T}}{T_{\rm ext}}-1\right)\\
\frac{d\eta(t)}{dt} &= \frac{1}{\mathcal{N}k_BT_{\rm ext}\tau_P^2}V(t)(\mathcal{P}-P_{\rm ext})\\
\frac{dV(t)}{dt} &= [3\eta(t)]V(t)
\end{aligned} \tag{2.174}$$

where η is the barostat friction coefficient, R_0 the system centre of mass, τ_P a specified time constant for pressure fluctuations, $\mathcal{P}$ the instantaneous pressure and V the system volume.

The conserved quantity is, to within a constant, the Gibbs free energy of the system:

$$\mathcal{H}_{NPT} = \mathcal{H}_{NVT} + P_{\rm ext}V(t) + \frac{3\mathcal{N}k_BT_{\rm ext}}{2}\eta(t)^2\tau_P^2 \tag{2.175}$$

The algorithm is readily implemented in the leapfrog scheme:

$$\begin{aligned}
\chi(t+\tfrac{1}{2}\Delta t) &\leftarrow \chi(t-\tfrac{1}{2}\Delta t)+\frac{\Delta t}{\tau_T^2}\left(\frac{\mathcal{T}}{T_{\rm ext}}-1\right)\\
\chi(t) &\leftarrow \frac{1}{2}\left[\chi(t-\tfrac{1}{2}\Delta t)+\chi(t+\tfrac{1}{2}\Delta t)\right]\\
\eta(t+\tfrac{1}{2}\Delta t) &\leftarrow \eta(t-\tfrac{1}{2}\Delta t)+\frac{\Delta t V(t)}{\mathcal{N}k_BT_{\rm ext}\tau_P^2}(\mathcal{P}-P_{\rm ext})\\
\eta(t) &\leftarrow \frac{1}{2}\left[\eta(t-\tfrac{1}{2}\Delta t)+\eta(t+\tfrac{1}{2}\Delta t)\right]\\
\underline{v}(t+\tfrac{1}{2}\Delta t) &\leftarrow \underline{v}(t-\tfrac{1}{2}\Delta t)+\Delta t\left[\frac{\underline{f}(t)}{m}-[\chi(t)+\eta(t)]\,\underline{v}(t)\right]\\
\underline{v}(t) &\leftarrow \frac{1}{2}\left[\underline{v}(t-\tfrac{1}{2}\Delta t)+\underline{v}(t+\tfrac{1}{2}\Delta t)\right]\\
\underline{r}(t+\Delta t) &\leftarrow \underline{r}(t)+\Delta t\left(\underline{v}(t+\tfrac{1}{2}\Delta t)+\eta(t+\tfrac{1}{2}\Delta t)\left[\underline{r}(t+\tfrac{1}{2}\Delta t)-\underline{R}_0\right]\right)\\
\underline{r}(t+\tfrac{1}{2}\Delta t) &\leftarrow \frac{1}{2}\left[\underline{r}(t)+\underline{r}(t+\Delta t)\right]
\end{aligned} \tag{2.176}$$

Like the Nosé-Hoover thermostat, several iterations are required to obtain self consistency. DL_POLY_2 uses 4 iterations (5 if bond constraints are present) with the standard Verlet leapfrog predictions for the initial estimates of $\mathcal{T}$, $\mathcal{P}$, $\underline{v}(t)$ and $\underline{r}(t+\frac{1}{2}\Delta t)$. Note also that the change in box size requires the SHAKE algorithm to be called each iteration with the new cell vectors obtained from:

$$\begin{aligned}
V(t+\Delta t) &\leftarrow V(t)\exp\left[3\Delta t\;\eta(t+\tfrac{1}{2}\Delta t)\right]\\
\underline{\underline{\mathbf{H}}}(t+\Delta t) &\leftarrow \underline{\underline{\mathbf{H}}}(t)\exp\left[\Delta t\;\eta(t+\tfrac{1}{2}\Delta t)\right]
\end{aligned} \tag{2.177}$$

where $\underline{\underline{\mathbf{H}}}$ is the cell matrix whose columns are the three cell vectors $\underline{a},\underline{b},\underline{c}$.

The isotropic changes to cell volume are implemented in the DL_POLY routine NPT_H1 which allows for systems containing bond constraints.

Cell size and shape variation

The isotropic algorithm may be extended to allowing the cell shape to vary by defining η as a tensor, $\underline{\underline{\eta}}$. The equations of motion are implemented as:

$$\begin{aligned}
\chi(t+\tfrac{1}{2}\Delta t) &\leftarrow \chi(t-\tfrac{1}{2}\Delta t) + \frac{\Delta t}{\tau_T^2}\left(\frac{\mathcal{T}}{T_{\rm ext}} - 1\right) \\
\chi(t) &\leftarrow \frac{1}{2}\left[\chi(t-\tfrac{1}{2}\Delta t) + \chi(t+\tfrac{1}{2}\Delta t)\right] \\
\underline{\underline{\eta}}(t+\tfrac{1}{2}\Delta t) &\leftarrow \underline{\underline{\eta}}(t-\tfrac{1}{2}\Delta t) + \frac{\Delta t V(t)}{\mathcal{N}k_B T_{\rm ext}\tau_P^2}\left(\underline{\underline{\sigma}} - P_{\rm ext}\underline{\underline{\mathbf{1}}}\right) \\
\underline{\underline{\eta}}(t) &\leftarrow \frac{1}{2}\left[\underline{\underline{\eta}}(t-\tfrac{1}{2}\Delta t) + \underline{\underline{\eta}}(t+\tfrac{1}{2}\Delta t)\right] \\
\underline{v}(t+\tfrac{1}{2}\Delta t) &\leftarrow \underline{v}(t-\tfrac{1}{2}\Delta t) + \Delta t\left[\frac{\underline{f}(t)}{m} - \left[\chi(t)\underline{\underline{\mathbf{1}}} + \underline{\underline{\eta}}(t)\right]\underline{v}(t)\right] \\
\underline{v}(t) &\leftarrow \frac{1}{2}\left[\underline{v}(t-\tfrac{1}{2}\Delta t) + \underline{v}(t+\tfrac{1}{2}\Delta t)\right] \\
\underline{r}(t+\Delta t) &\leftarrow \underline{r}(t) + \Delta t\left(\underline{v}(t+\tfrac{1}{2}\Delta t) + \underline{\underline{\eta}}(t+\tfrac{1}{2}\Delta t)\left[\underline{r}(t+\tfrac{1}{2}\Delta t) - \underline{R}_0\right]\right) \\
\underline{r}(t+\tfrac{1}{2}\Delta t) &\leftarrow \frac{1}{2}\left[\underline{r}(t) + \underline{r}(t+\Delta t)\right]
\end{aligned} \tag{2.178}$$

where $\underline{\underline{\mathbf{1}}}$ is the identity matrix and $\underline{\underline{\sigma}}$ the pressure tensor. The new cell vectors are calculated from

$$\underline{\underline{\mathbf{H}}}(t+\Delta t) \leftarrow \underline{\underline{\mathbf{H}}}(t)\exp\left[\Delta t\,\underline{\underline{\eta}}(t+\tfrac{1}{2}\Delta t)\right] \tag{2.179}$$

DL_POLY_2 uses a power series expansion truncated at the quadratic term to approximate the exponential of the tensorial term. The new volume is found from

$$V(t+\Delta t) \leftarrow V(t)\exp\left[\Delta t\,\mathrm{tr}(\underline{\underline{\eta}})\right] \tag{2.180}$$

The conserved quantity is

$$\mathcal{H}_{NPT} = \mathcal{H}_{NVT} + P_{\rm ext}V(t) + \frac{3\mathcal{N}k_B T_{\rm ext}}{2}\mathrm{tr}[\underline{\underline{\eta}}(t)]^2\tau_P^2 \tag{2.181}$$

This algorithm is implemented in the routines NST_H0 (nonbonded systems) and NPT_H3 (with bond constraints).

2.5.5.2 Berendsen Barostat

With the Berendsen barostat the system is made to obey the equation of motion

$$\frac{d\mathcal{P}}{dt} = (P_{\rm ext} - \mathcal{P})/\tau_P \tag{2.182}$$

Cell size variations

In the isotropic implementation, at each step the MD cell volume is scaled by by a factor η and the coordinates, and cell vectors, by $\eta^{1/3}$ where

$$\eta = 1 - \frac{\beta\Delta t}{\tau_P}(P_{\rm ext} - \mathcal{P}) \tag{2.183}$$

and β is the isothermal compressibility of the system. The Berendesen thermostat is applied at the same time. In practice β is a specified constant which DL_POLY_2 takes to be the isothermal compressibility of liquid water. The exact value is not critical to the algorithm as it relies on the ratio τ_P/β. τ_P is specified by the user.

This algorithm is implemented in NPT_B1 with 4 or 5 iterations used to obtain self consistency in the $\underline{v}(t)$.

Cell size and shape variations

The extension of the isotropic algorithm to anisotropic cell variations is straightforward. The tensor $\underline{\underline{\eta}}$ is defined by

$$\underline{\underline{\eta}} = \underline{\underline{\mathbf{1}}} - \frac{\beta\Delta t}{\tau_P}(P_{\rm ext}\underline{\underline{\mathbf{1}}} - \underline{\underline{\sigma}}) \tag{2.184}$$

and the new cell vectors given by

$$\underline{\underline{\mathbf{H}}}(t+\Delta t) \leftarrow \underline{\underline{\mathbf{H}}}(t)\underline{\underline{\eta}} \tag{2.185}$$

As in the isotropic case the Berendsen thermostat is applied simultaneously and 4 or 5 iterations are used to obtain convergence. The algorithm is implemented in NST_B0 (nonbonded systems) and NPT_B3 (with bond constraints).

2.5.6 Rigid Bodies and Rotational Integration Algorithms

2.5.6.1 Description of Rigid Body Units

A rigid body unit is a collection of point atoms whose local geometry is time invariant. One way to enforce this in a simulation is to impose a sufficient number of bond constraints between the atoms in the unit. However, in many cases this is may be either problematic or impossible. Examples in which it is impossible to specify sufficient bond constraints are

1. linear molecules with more than 2 atoms (e.g. CO_2)
2. planar molecules with more than three atoms (e.g. benzene).

Even when the structure *can* be defined by bond constraints the network of bonds produced may be problematic. Normally, they make the iterative SHAKE procedure slow, particularly if a ring of constraints is involved (as occurs when one defines water as a constrained triangle). It is also possible, inadvertently, to over constrain a molecule (e.g. by defining a methane tetrahedron to have 10 rather than 9 bond constraints) in which case the SHAKE procedure will become unstable. In addition, massless sites (e.g. charge sites) cannot be included in a simple constraint approach making modelling with potentials such as TIP4P water impossible. All these problems may be circumvented by defining rigid body units in terms of a center of mass (c.o.m) and an orientation and solving the resultant rigid body equations of motion. [4]

A rigid body has associated with it a rotational inertia matrix $\underline{\underline{\mathbf{I}}}$, whose components are given by $I_{\alpha\beta} = 1/2 \sum_{\text{sites}} m r_\alpha r_\beta$ where the r are the distance to the centre of mass and the m are the site masses. In DL_POLY_2 we define the local body frame to be that in which the rotational inertia tensor $\hat{\underline{\underline{\mathbf{I}}}}$ is diagonal and the components satisfy $I_{xx} \geq I_{yy} \geq I_{zz}$. These three components are stored in the arrays `rotinx`, `rotiny` and `rotinz` for each unique type of rigid body in the system. The total mass of the rigid body unit, M, is stored in the array `gmass` and the location of sites with respect to the local body axes are stored in the arrays `gxx`, `gyy` and `gzz`.

The orientation of a local body frame with respect to the space fixed frame is described via a four dimensional unit vector, the quaternion $\underline{q} = [q_0, q_1, q_2, q_3]^T$. The Rotational matrix to transform from the local body frame to the space fixed frame is the unitary matrix

$$\underline{\underline{\mathbf{R}}} = \begin{pmatrix} q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2(q_1 q_2 - q_0 q_3) & 2(q_1 q_3 + q_0 q_2) \\ 2(q_1 q_2 + q_0 q_3) & q_0^2 - q_1^2 + q_2^2 - q_3^2 & 2(q_2 q_3 - q_0 q_1) \\ 2(q_1 q_3 - q_0 q_2) & 2(q_2 q_3 + q_0 q_1) & q_0^2 - q_1^2 - q_2^2 + q_3^2 \end{pmatrix} \tag{2.186}$$

so that if $\hat{\underline{d}}_\alpha$ is the position of a site in the local body frame with respect to its centre of mass, its position in the space fixed frame (w.r.t. its centre of mass) is given by

$$\underline{d}_\alpha = \underline{\underline{\mathbf{R}}}\, \hat{\underline{d}}_\alpha \tag{2.187}$$

2.5.6.2 Integration of the Rigid Body Equations of Motion

The net translational force acting upon the rigid unit is

$$\underline{F} = \sum_\alpha \underline{f}_\alpha \tag{2.188}$$

where $\underline{f}_\alpha$ is the force on a rigid unit site, and the sum includes all sites α in the body. The translational motion can be integrated by the standard leapfrog algorithm.

$$\underline{V}(t + \frac{\Delta t}{2}) = \underline{V}(t - \frac{\Delta t}{2}) + \Delta t\, M^{-1} \underline{F}(t) \tag{2.189}$$

[4] An alternative approach is to define "basic" and "secondary" particles. The basic particles are the minimun number needed to define a local body axis system. The remaining particle positions are expressed in terms of the c.o.m. and the basic particles. Ordinary bond constraints can then be applied to the basic particles provided the forces and torques arising from the secondary particles are transferred to the basic particles in a physically meaningful way.

$$\underline{X}(t+\Delta t) = \underline{X}(t) + \Delta t\, \underline{V}(t+\frac{\Delta t}{2}) \tag{2.190}$$

where M is the mass of the rigid unit, $\underline{V}$ is the rigid bodies c.o.m. velocity and $\underline{X}$ is the c.o.m. position. The cartesian components of these quantitites are stored in the arrays: `gvxx`, `gvyy`, and `gvzz` for c.o.m. velocity; and `gcmx`, `gcmy`, and `gcmz` for c.o.m. position.

The torque acting upon the body in the space fixed frame is

$$\underline{\tau} = \sum_{\alpha} \underline{d}_{\alpha} \times \underline{f}_{\alpha}. \tag{2.191}$$

Transformed to the local body frame (and including the centrifugal terms) this is

$$\hat{\underline{\tau}} = \underline{\underline{\mathbf{R}}}^{T}\, \underline{\tau} + \underline{eta}. \tag{2.192}$$

where

$$\eta_x = (\hat{I})_{yy} - \hat{(I)}_{zz})\hat{\omega}_y\hat{\omega}_z \tag{2.193}$$

plus cyclic permutations for y and z components. The angular velocity transformed to the local body frame, $\hat{\omega}$, can then be integrated using the leapfrog algorithm and the diagonal rotational inertia tensor.

$$\hat{\omega}(t+\frac{\Delta t}{2}) = \hat{\omega}(t-\frac{\Delta t}{2}) + \Delta t\, \underline{\underline{\hat{\mathbf{I}}}}^{-1}\, \hat{\underline{\tau}}(t) \tag{2.194}$$

The new quaternions cannot be found so simply. DL_POLY_2 uses Fincham's implicit quaternion algorithm (FIQA) to do this [12]. In this algorithm the new quaternions are found by solving the implicit equation

$$\underline{q}(t+\Delta t) = \underline{q}(t) + \frac{\Delta t}{2}\, \left(\underline{\underline{\mathbf{Q}}}[\underline{q}(t)]\underline{\hat{w}}(t) + \underline{\underline{\mathbf{Q}}}[\underline{q}(t+\Delta t)]\underline{\hat{w}}(t+\Delta t)\right) \tag{2.195}$$

where $\underline{\hat{w}} = [0, \hat{\omega}]^T$ and $\underline{\underline{\mathbf{Q}}}[\underline{q}]$ is

$$\underline{\underline{\mathbf{Q}}} = \frac{1}{2}\begin{pmatrix} q_0 & -q_1 & -q_2 & -q_3 \\ q_1 & q_0 & -q_3 & -q_2 \\ q_2 & q_3 & q_0 & -q_1 \\ q_3 & -q_2 & q_1 & q_0 \end{pmatrix} \tag{2.196}$$

The above equation is solved iteratively with

$$\underline{q}(t+\Delta t) = \underline{q}(t) + \Delta t\, \underline{\underline{\mathbf{Q}}}[\underline{q}(t)]\underline{\hat{w}}(t) \tag{2.197}$$

as the first guess. Typically no more than 3 or 4 iterations are needed for convergence. At each step the constraint

$$\|\underline{q}(t+\Delta t)\| = 1 \tag{2.198}$$

is imposed.

The quaternions are stored in the arrays `q0, q1, q2` and `q3`. The angular velocity (transformed to the body fixed frame) is stored in the arrays `omx, omy` and `omx`, while

the work arrays `opx, opy, opz, oqx, oqy, oqz` hold values of $\hat{\omega}(t)$ and $\hat{\omega}(t+\Delta t)$. The torques, $\hat{\tau}(t)$ are held in the work arrays `tqx, tqy` and `tqz`.

The NVE algorithm is implemented in NVEQ_1 which allows for a system containing a mixture of rigid bodies and atomistic species, provided the rigid bodies are not linked to other species by constraint bonds.

Thermostats and Barostats

It is straightforward to couple the rigid body equations of motion to a thermostat and/or barostat. The thermostat is coupled to both the translational and rotational degrees of freedom and so both the translational and rotational velocities are propagated in an analogous manner to the thermostated atomic velocities. The barostat, however, is coupled only to the translational degrees of freedom, not to the rotational ones.DL_POLY_2 supports both Hoover type and Berendsen thermostats and barostats for systems containing rigid bodies. The Hoover thermostat is implemented in NVTQ_H1, the Hoover isotropic barostat (plus themostat) in NPTQ_H1 and the anisotropic barostat in NPTQ_H3. The analogous routines for the Berendsen algorithms are NVTQ_B1, NPTQ_B1 and NPTQ_B3.

2.5.6.3 Linked Rigid Bodies

The above integration algorithm can be used for rigid bodies in a system containing "atomic" species (whose equations of motion are integrated with the standard leapfrog algorithm). These rigid bodies may even be linked to other species (including other rigid bodies) by extensible bonds. However if a rigid body is linked to an atom or another rigid body by a bond *constraint* the above algorithm is not adequate. The reason is that the constraint will introduce an additional force and torque onto the body that can only be found *after* the integration of the unconstrained unit. DL_POLY_2 has a suite of integration algorithms to cope with this situation in which both the constraint conditions and the quaternion equations are solved similtaneously using an extension of the SHAKE algorithm called "QSHAKE" [13].

The QSHAKE algorithm proceeds as follows: Consider the figure in which two rigid bodies are linked by a constraint bond. We seek to choose $\underline{F}_{\rm const}$ so that at the end of the integration step the two sites in the constraint bond are a distance r apart. The integration of the bodies as free units leaves the sites r' apart. Since the constraint force produces both a force and torque on the rigid units the correction to the constrained sites position must include both the translation and rotation of the body as a whole. The translational contribution is

$$\Delta\underline{x}_T = (\Delta t)^2 \underline{F}_{\rm const}\left(\frac{1}{M}\right) \tag{2.199}$$

The torque induced by the constraint force is

$$\underline{\tau}_{\rm const} = \underline{d}_a \times \underline{F}_{\rm const} \tag{2.200}$$

so the correction to the angular velocity of the body is

$$\Delta\underline{\omega} = \Delta t\ \underline{\underline{\mathbf{I}}}^{-1}\ \underline{\tau}_{\rm const}. \tag{2.201}$$

The "rotational" correction to the position of the site is thus

$$\Delta\underline{x}_R = \Delta t\ (\Delta\underline{\omega} \times \underline{d}_a) \tag{2.202}$$

which in general will not be in the same direction as $\underline{F}_{\rm const}$ and $\Delta\underline{x}_T$. If we denote the components of $\Delta\underline{x}_R$ parallel and perpendicular to $\underline{F}_{\rm const}$ by $\Delta\underline{x}_R^{\parallel}$ and $\Delta\underline{x}_R^{\perp}$ the correction to the site position is

$$\Delta\underline{x} = (\Delta\underline{x}_T + \Delta\underline{x}_R^{\parallel}) + \Delta\underline{x}_R^{\perp} \tag{2.203}$$

Clearly the presence of the constraint force and torque will mean the positions and velocities of the remaining sites in the rigid body will also have to be corrected. We proceed by seeking an *approximation* to $\underline{F}_{\rm const}$ then reintegrating the rigid body equations of motion with the improved total forces and torques on the body. A few iterations are normally sufficient to achieve convergence: If we assume the bond distance r is large in comparison to the correction then after the correction is made the bond length is

$$\begin{aligned} r^* &= \sqrt{\left[\left(r' + \Delta x_{\parallel}\right)^2 + (\Delta x_{\perp})^2\right]} \\ &= \sqrt{\left[(r')^2 + 2r'\Delta x_{\parallel} + \Delta x_{\parallel}^2 + \Delta x_{\perp}^2\right]} \\ &\approx \sqrt{\left[(r')^2 + 2r'\Delta x_{\parallel}\right]} \end{aligned} \tag{2.204}$$

$$\tag{2.205}$$

where $\Delta x_{\parallel} = \sum_{\rm bodies} \Delta x_T + \Delta x_R^{\parallel}$ and $\Delta x_{\perp} = \sum_{\rm bodies} \Delta x_R^{\perp}$. Thus a first order correction to the position of the constrained site is

$$\begin{aligned} \Delta\underline{x} &= \Delta\underline{x}_T + \Delta\underline{x}_R^{\parallel} \\ &= (\Delta t)^2 \underline{F}_{\rm const} \left\{ \frac{1}{M} + \left[\left(\underline{\underline{\mathbf{I}}}^{-1}\,(\underline{d}_a \times \underline{e})\right) \times \underline{d}_a\right] \cdot \underline{e} \right\} \end{aligned} \tag{2.206}$$

where $\underline{e}$ is the unit vector $\underline{F}_{\rm const}/\|\underline{F}_{\rm const}\|$. The term in the $\{\ldots\}$ defines an effective mass, $\mathcal{M}$: where $1/\mathcal{M} = 1/M + \left[\left(\underline{\underline{\mathbf{I}}}^{-1}\,(\underline{d}_a \times \underline{e})\right) \times \underline{d}_a\right] \cdot \underline{e}$.

The effective reduced mass for the two linked bodies, a and b, is $\mu = \mathcal{M}_a\mathcal{M}_b/(\mathcal{M}_a+\mathcal{M}_b)$. As in the standard SHAKE algorithm, the reduced mass can then be used to predict the constraint force

$$F_{\rm const} = \frac{\mu}{\Delta t^2}\frac{(r^2 - r'^2)}{2r^2} \tag{2.207}$$

Note that each prediction of the constraint force requires the rigid body equations of motion to be reintegrated accurately. If two bodies are linked by one constraint bond only two or three iterations are necessary for convergence. However convergence may be slower if an extended network of linked bodies is involved. Note also that the reduced mass needs to be re-evaluated every time-step because it depends on the relative orienation of the two bodies. Finally, we note the algorithm reduces to the standard SHAKE algorithm if the rigid bodies are replaced by point atoms. In such a case, even though d_a is zero, care must be taken to avoid the singularity arising from $\underline{\underline{\mathbf{I}}}^{-1}$.

This "linked rigid body" algorithm is implemented in NVEQ_2 with the QSHAKE corrections to the forces applied in QSHAKE. Again it is straightforward to couple these systems to a Hoover type or Berendsen thermostat and/or barostat. The Hoover and Berendsen thermostated versions are found in NVTQ_H2 and NVTQ_B2 respectively. The isotropic constant pressure implementations are found in NPTQ_H2 and NPTQ_B2, while the anisotropic constant pressure routines are found in NPTQ_H4 and NPTQ_B4. An outline of the parallel version of QSHAKE is given in section 2.6.8.

2.5.7 The DL_POLY_2 Multiple Timestep Algorithm

For simulations employing a large spherical cutoff r_{cut} in the calculation of the interactions DL_POLY_2 offers the possibility of using a multiple timestep algorithm to improve the efficiency. The method is based on that described by Streett *et al* [38, 39] with extension to Coulombic systems by Forester *et al* [40].

In themultiple timestep algorithm there are two cutoffs for the pair interactions: a relatively large cutoff (r_{cut}) which is used to define the standard Verlet neighbour list; and a smaller cutoff r_{prim} which is used to define a *primary list* within the larger cutoff sphere (see figure). Forces derived from atoms in the primary list are generally much larger than those derived from remaining (so-called *secondary*) atoms in the neighbour list. Good energy conservation is therefore possible if the forces derived from the primary atoms are calculated *every* timstep, while those from the secondary atoms are calculated much less frequently, and are merely extrapolated over the interval. DL_POLY_2 handles this procedure as follows.

DL_POLY_2 updates the Verlet neighbour list at irregular intervals, determined by the movement of atoms in the neighbour list (see section 2.1). The interval between updates is usually of the order of ∼20 timesteps. Partitioning the Verlet list into primary and secondary atoms always occurs when the Verlet list is updated, and thereafter at intervals of `multt` timesteps (i.e. the multi-step interval specified by the user - see section 4.1.1). Immediately after the partitioning, the force contributions from both the primary and secondary atoms are calculated. The forces are again calculated *in total* in the subsequent timestep. Thereafter, for `multt`-2 timesteps, the forces derived from the primary atoms are calculated explicitly, while those derived from the secondary atoms are calculated by linear extrapolation of the exact forces obtained in the first two timesteps of the multi-step interval. It is readily apparent how this scheme can lead to a significant saving in execution time.

Extension of this basic idea to simulations using the Ewald sum requires the following:

1. the reciprocal space terms are calculated only for the first two timesteps of the multi-step,

2. the contribution to the reciprocal space terms arising from primary interactions are immediately subtracted, leaving only the long-range components. (This is done in real space, by subtracting *erf* terms.);

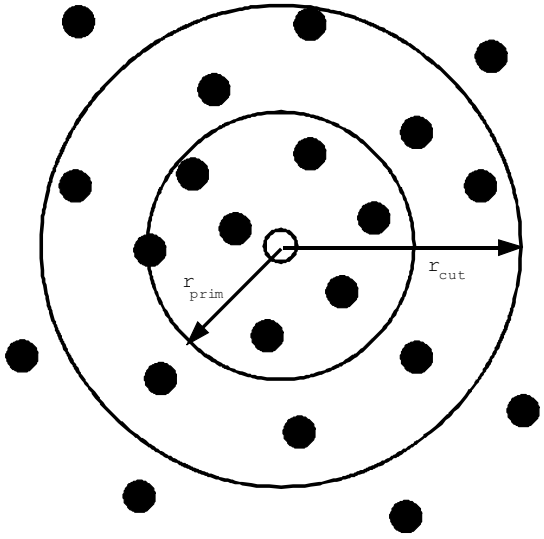
3. the real space Coulombic forces arising from the secondary atoms are calculated in

the first two timesteps of the multi-step using the normal Ewald expressions (i.e. the *erfc* terms).

4. the Coulombic forces arising from primary atoms are calculated at every timestep in real space assuming the *full Coulombic force*;

In this way the Coulombic forces can be handled by the same multiple timestep scheme as the van der Waals forces. The algorithm is described in detail in [40].

Note that the accuracy of the algorithm is a function of the multi-step interval `multt`, and decreases as `multt` increases. Also, the algorithm is *non-symplectic* (i.e. it is not time reversible) and is therefore susceptible to energy drift. Its use with a thermostat is therefore advised.



dius r_{prim} and secondary if outside this radius but within r_{cut}. Interactions arising from primary atoms are evaluated every time

2.5.8 The DL_POLY_2 RESPA Multiple Timestep Implementation

The DL_POLY_2 RESPA Program is a variant of DL_POLY_2 that handles the time reversible, multiple timestep RESPA algorithm due to Tuckerman and Berne [17, 18] as implemented by Procacci and Marchi for atomic and rigid ion systems[19]. However, it is not applicable to systems which have rigid body molecules or constraints, and for this reason the RESPA code is kept separate from the DL_POLY_2 main source in the sub-directory called *respa*.

The DL_POLY_2 implementation allows the user to define three concentric regions around a given atom. Forces deriving from atoms in the innermost region are updated more frequently (i.e. every timestep) than those in the immediate outer region, which in turn are updated more frequently than those deriving from the outermost region. This (depending on the relative sizes of each region and the frequency of the forces update)

can represent a great computational saving. This is coupled with the advantage that the algorithm is time reversible and therefore possesses long term stability.

The method is fully documented in [19]. A makefile (Makefile_respa) is available in the *build sub-directory*, which will build the RESPA program (DLRESPA.X). A test case may be found in the *data* sub-directory.

2.6 DL_POLY Parallelisation

DL_POLY_2 is a distributed parallel molecular dynamics package based on the Replicated Data parallelisation strategy [41, 42]. In this section we briefly outline the basic methodology. Users wishing to add new features DL_POLY_2 will need to be familiar with the underlying techniques as they are described (in greater detail) in references [30, 42]).

2.6.1 The Replicated Data Strategy

The Replicated Data (RD) strategy [41] is one of several ways to achieve parallelisation in MD. Its name derives from the replication of the configuration data on each node of a parallel computer (i.e. the arrays defining the atomic coordinates $\underline{r}_i$, velocities $\underline{v}_i$ and forces $\underline{f}_i$, for all N atoms $\{i : i = 1, \ldots, N\}$ in the simulated system, are reproduced on every processing node). In this strategy most of the forces computation and integration of the equations of motion can be shared easily and equally between nodes and to a large extent be processed independently on each node. The method is relatively simple to program and is reasonably efficient. Moreover, it can be "collapsed" to run on a single processor very easily. However the strategy can be expensive in memory and have high communication overheads, but overall it has proven to be successful over a wide range of applications. These issues are explored in more detail in [41, 42].

Systems containing complex molecules present several difficulties. They often contain ionic species, which usually require Ewald summation methods [10, 43], and *intra*-molecular interactions in addition to *inter*-molecular forces. These are handled easily in the RD strategy, though the SHAKE algorithm [11] requires significant modification [30].

The RD strategy is applied to complex molecular systems as follows:

1. Using the known atomic coordinates $\underline{r}_i$, each node calculates a subset of the forces acting between the atoms. These are usually comprised of:
   (a) atom-atom pair forces (e.g. Lennard Jones, Coulombic etc.);
   (b) non-rigid atom-atom bonds;
   (c) valence angle forces;
   (d) dihedral angle forces;
   (e) improper dihedral angle forces.
2. The computed forces are accumulated in (incomplete) atomic force arrays $\underline{f}_i$ independently on each node;

3. The atomic force arrays are summed globally over all nodes;

4. The complete force arrays are used to update the atomic velocities and positions.

It is important to note that load balancing (i.e. equal and concurrent use of all processors) is an essential requirement of the overall algorithm. In DL_POLY_2 this is accomplished for the pair forces with an adaptation of the Brode-Ahlrichs scheme [22].

2.6.2 Distributing the Intramolecular Bonded Terms

DL_POLY_2 handles the intramolecular in which the atoms involved in any given bond term are explicitly listed. Distribution of the forces calculations is accomplished by the following scheme:

1. Every atom in the simulated system is assigned a unique index number from 1 to N;

2. Every intramolecular bonded term U_{type} in the system has a unique index number i_{type}: from 1 to N_{type} where *type* represents a bond, angle or dihedral.

3. A pointer array $key_{type}(n_{type}, i_{type})$ carries the indices of the specific atoms involved in the potential term labelled i_{type}. The dimension n_{type} will be 2, 3 or 4, if the term represents a bond, angle or dihedral.

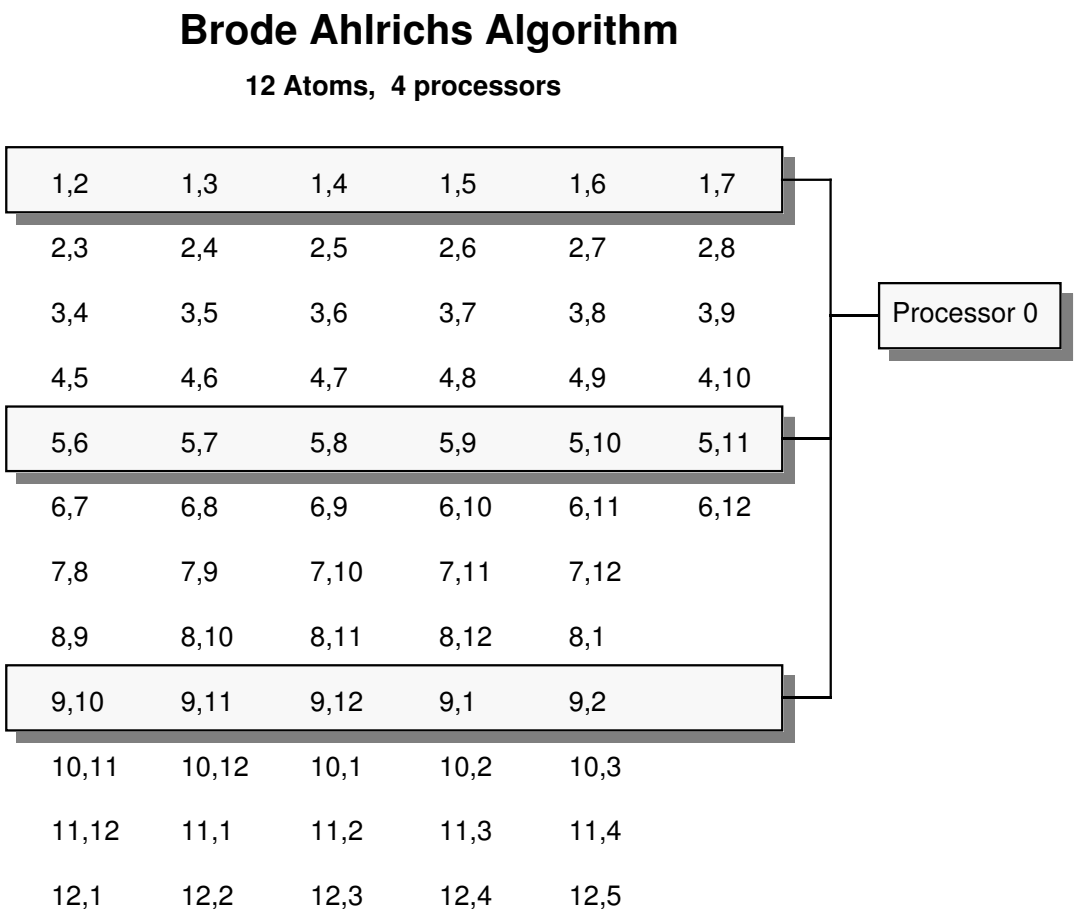
4. The array $key_{type}(n_{type}, i_{type})$ is used to identify the atoms in a bonded term and the appropriate form of interaction and thus to calculate the energy and forces. Each processor is assigned the independent task of evaluating a block of $(Int(N_{total}/N_{nodes}))$ interactions.

The same scheme works for all types of bonded interactions. The global summation of the force arrays does not occur until all the force contributions, including nonbonded forces has been completed.

2.6.3 Distributing the Nonbonded Terms

In DL_POLY_2 the nonbonded interactions are handled with a Verlet neighbour list [10] which is reconstructed at intervals during the simulation. This list records the indices of all 'secondary' atoms within a certain radius of each 'primary' atom; the radius being the cut-off radius (r_{cut}) normally applied to the nonbonded potential function, plus an additional increment (Δr_{cut}). The larger radius ($r_{cut} + \Delta r_{cut}$) permits the same list to be used for several timesteps without requiring an update. The frequency at which the list must be updated clearly depends on the thickness of the region Δr_{cut}. In RD, the neighbour list is constructed *simultaneously* on each node and in such a way as to share the total burden of the work equally between nodes. Each node is responsible for a unique set of nonbonded interactions and the neighbour list is therefore different on each node. DL_POLY_2 uses a method based on the Brode-Ahlrichs scheme [22] (see figure below) to construct the neighbour list.

Additional modifications are necessary to handle the excluded atoms [42]. A distributed *excluded atoms list* is constructed by DL_POLY_2 at the start of the simulation. The list is constructed so that the excluded atoms are referenced in the same order as they would appear in the Verlet neighbour list if the bonded interactions were ignored, allowing for the distributed structure of the neighbour list.



Schematic diagram of the parallel implementation of the Brode-Ahlrichs algorithm.

The diagram illustrates the reordering of the upper triangular matrix of n(n-1)/2 pair interactions so that the rows of the matrix are of approximately equally length. Each entry in the table consists of a primary atom index (constant within a row) and a "neighbouring" atom index. Rows are assigned sequentially to nodes. In the diagram node 0 deals with rows 1, 5 and 9, node 1 to rows 2, 6, and 10 etc.

When a charge group scheme (as opposed to an atomistic scheme) is used for the non-bonded terms, the group-group interactions are distributed using the Brode-Ahlrichs approach. This makes the Verlet list considerably smaller, thus saving memory, but also results in a more "coarse grain" parallelism. The consequence of which is that performance

with a large number of processors will degrade more quickly than with the atomistic scheme.

Once the neighbour list has been constructed, each node of the parallel computer may proceed independently to calculate the pair force contributions to the atomic forces.

2.6.4 Modifications for the Ewald Sum

For systems with periodic boundary conditions DL_POLY_2 employs the Ewald Sum to calculate the Coulombic interactions (see section 2.4.5).

Calculation of the real space component in DL_POLY_2 employs the algorithm for the calculation of the nonbonded interactions outlined above. The reciprocal space component is calculated using the schemes described in [43], in which the calculation can be parallelised by distribution of either $\underline{k}$ vectors or atomic sites. Distribution over atomic sites requires the use of a global summation of the $q_i \exp(-i\underline{k} \cdot \underline{r}_j)$ terms, but is more efficient in memory usage. Both strategies are computationally straightforward. Subroutine EWALD1 distributes over atomic sites and is often the more efficient of the two approaches. Subroutine EWALD1A distributes over the $\underline{k}$ vectors and may be more efficient on machines with large communication latencies.

Other routines required to calculate the ewald sum include EWALD2, EWALD3 and EWALD4. The first of these calculates the real space contribution, the second the self interaction corrections, and the third is required for the multiple timestep option.

2.6.5 Three Body Forces

DL_POLY_2 can calculate three body interactions of the valence angle type [44]. These are not dealt with in the same way as the normal nonbonded interactions. They are generally very short ranged and are most effectively calculated using a link-cell scheme [23]. No reference is made to the Verlet neighbour list nor the excluded atoms list. It follows that atoms involved in the same three-body term can interact via nonbonded (pair) forces and ionic forces also. The calculation of the three-body terms is distributed over processors on the basis of the identity of the central atom in the bond. A global summation is required to specify the atomic forces fully.

2.6.6 Metal Potentials

The simulation of metals by DL_POLY_2 makes use of density dependent potentials of the Sutton-Chen type [6]. The dependence on the atomic density presents no difficulty however, as this class of potentials can be resolved into pair contributions. This permits the use of the distributed Verlet neighbour list outlined above.

2.6.7 Summing the Atomic Forces

The final stage in the RD strategy, is the global summation of the atomic force arrays. This must be done After all the contributions to the atomic forces have been calculated. To do this DL_POLY_2 employs a global summation algorithm [41], which is generally a system specific utility.

Similarly, the total configuration energy and virial must be obtained as a global sum of the contributing terms calculated on all nodes.

2.6.8 The RD-SHAKE and Parallel QSHAKE Algorithms

The RD-SHAKE algorithm is a parallel adaptation of SHAKE couched in the Replicated Data strategy. The essentials of the RD-SHAKE method are as follows.

1. The bond constraints acting in the simulated system are shared equally between the processing nodes.
2. Each node makes a list recording which atoms are bonded by constraints it is to process. Entries are zero if the atom is not bonded.
3. A copy of the array is passed to each other node in turn. The receiving node compares the incoming list with its own and keeps a record of the shared atoms and the nodes which share them.
4. In the first stage of the SHAKE algorithm, the atoms are updated through the usual Verlet algorithm, without regard to the bond constraints.
5. In the second (iterative) stage of SHAKE, each node calculates the incremental correction vectors for the bonded atoms in its own list of bond constraints. It then sends specific correction vectors to all neighbours that share the same atoms, using the information compiled in step 3.
6. When all necessary correction vectors have been received and added the positions of the constrained atoms are corrected.
7. Steps 5 and 6 are repeated until the bond constraints are converged.
8. After convergence the coordinate arrays on each node are passed to all the other nodes. The coordinates of atoms that are *not* in the constraint list of a given node are taken from the incoming arrays (an operation we term *splicing*).
9. Finally, the change in the atom positions is used to calculate the atomic velocities.

This scheme contains a number of non-trivial operations, which are described in detail in [30]. However some general comments are worth making.

The compilation of the list of constrained atoms on each node, and the circulation of the list (items 1 - 3 above) need only be done once in any given simulation. It also transpires that in sharing bond contraints between nodes, there is an advantage to keeping as many of the constraints pertaining to a particular molecule together on one node as is possible within the requirement for load balancing. This reduces the data that need to be transferred between nodes during the iteration cycle. It is also advantageous, if the molecules are small, to adjust the load balancing between processors to prevent shared atoms. The loss of balance is compensated by the elimination of communications during the SHAKE cycle. These techniques are exploited by DL_POLY_2 .

The QSHAKE algorithm is an extension of the SHAKE algorithm for constraint bonds between rigid bodies. The parallel strategy is very similar to that of RD-SHAKE. The only significant difference is that increments to the atomic forces, not the atomic positions, are passed between processors at the end of each iteration.

Chapter 3

DL_POLY_2 Construction and Execution

Scope of Chapter

This chapter describes how to compile a working version of DL_POLY_2 and how to run it.

3.1 Constructing DL_POLY_2 : an Overview

3.1.1 Constructing the Standard Version

DL_POLY_2 was designed as a package of useful subroutines rather than a single program, which means that users were to be able to construct a working simulation program of their own design from the subroutines available, which is capable of performing a specific simulation. However we recognise that many, perhaps most, users will be content with creating a standard version that covers a wide variety (if not all) of the possible applications and for this reason we have provided the necessary tools to assemble such a version. The method of creating the standard version is described in detail in this chapter, however a brief step-by-step description follows.

1. DL_POLY_2 is supplied as a UNIX compressed tar file. This must uncompressed and un-tared to create the DL_POLY_2 directory (section 1.4).

2. In the *build* subdirectory you will find the required DL_POLY_2 makefile (see section 3.2.1 and Appendix A, where the main Makefile is listed). This must be copied into the subdirectory containing the relevant source code. In most cases this will be the *source* subdirectory.

3. The makefile is executed with the appropriate keywords (section 3.2.1) which select for specific computers and if a parallel machine is used, the appropriate communication software.

4. The makefile produces the executable version of the code, which as a default will be named DLPOLY.X and located in the *execute* subdirectory.

5. To run the executable for the first time you require the files CONTROL, FIELD and CONFIG (and possibly TABLE if you have tabulated potentials). These must be present in the directory from which the program is executed. (See section 4.1 for the description of the input files.)

6. Executing the program will produce the files OUTPUT, REVCON and REVIVE (and optionally STATIS, HISTORY, RDFDAT and ZDNDAT) in the executing directory. (See section 4.2 for the description of the output files.)

This simple procedure is enough to create a standard version to run the supplied test cases. (For versions preceeding 2.11, it will not run the larger benchmark cases however.) Creating a larger executable, or one which is tailored to an application different from the test cases is more complicated. The main difficulty centres on assigning appropriate array dimensions to meet the application's needs. In versions of DL_POLY_2 after 2.11 these dimensions are calculated by the subroutine PARSET.F and its support routines CFGSCAN.F, CONSCAN.F and FLDSCAN.F. These support routines scan the CONFIG, CONTROL and FIELD files at the start of a run and estimate the required array sizes. (A description of the individual arrays found in DL_POLY_2 is provided in Appendix C of the DL_POLY_2 Reference Manual.)

In versions preceeding 2.11, the size of the DL_POLY_2 executable is determined by the the DL_PARAMS.INC (include) file (see section 7.1.1), which specifies all the FORTRAN parameters of the code and is included in each subroutine at compile time. This file is found in the *source* directory and is internally documented (it is also documented in chapter 7). Reconstructing the DL_PARAMS.INC for a new simulation is the most difficult aspect of preparing a DL_POLY_2 executable. If the parameters are not appropriate, DL_POLY_2 will complain if any parameter is too small and abort in execution. Each such error will entail a recompilation of the code, and DL_POLY_2 generally detects only one error at a time! Fortunately, the process of creating a new DL_PARAMS.INC file is greatly assisted by the utility program PARSET (see section 6.1.1). Provided the CONTROL, CONFIG and FIELD files are available, PARSET will create a suitable parameters file for you. (See section 3.2.2).

3.1.2 Constructing Nonstandard Versions

In constructing a nonstandard DL_POLY_2 simulation program, the first requirement is for the user to write a program to function as the root segment. The *source* directory contains an example of such a root program: DLPOLY. This root program calls the major routines required to perform the simulation and also controls the normal "molecular dynamics cycle" which consists of forces calculation followed by integration of the equation of motion. DLPOLY also monitors the *cpu* usage and brings about a controlled termination of the program if the usage approaches the allotted job time within a pre-set closure time. Lastly, DLPOLY is the routine that first opens the OUTPUT file (section 4.2.2), which provides the summary of the job. Users are recommended to study the DLPOLY root as a model for other implementations of the package they may wish to construct. The dependencies and calling hierarchies of all the DL_POLY_2 subroutines can be found in the Appendix of the DL_POLY_2 Reference Manual.

If additional functionality is added to DL_POLY_2 by the user, the PARSET.F routine (and its support routines) will need modifying to allow specification of the dimensions of any new arrays. (A description of the existing arrays found in DL_POLY_2 is provided in the Appendix of the DL_POLY_2 Reference Manual.)

Any molecular dynamics simulation performs five different kinds of operation: initialisation; forces calculation; integration of the equations of motion; calculation of system properties; and job termination. It is worth considering these operations in turn and to indicate which DL_POLY_2 routines are available to perform them. We do not give a detailed description, but provide only a guide. Readers are recommended to examine the different routines described in chapter 7 of the DL_POLY_2 Reference Manual for further details (particularly regarding further dependencies i.e. additional routines that must be called.) The following outline assumes a system containing flexible molecules held together by rigid bonds, but without rigid bodies.

Initialisation requires firstly that the program determine what kind of parallel machine it is running on. The routine MACHINE determines how many processing nodes are being used and also returns the node identity to each process. Next the job control information is required; this is obtained by the routine SIMDEF, which reads the CONTROL file (section

4.1.1). The description of the system to be simulated: the types of atoms and molecules present and the intermolecular forces; are obtained by the SYSDEF routine, which reads the FIELD file (section 4.1.3). Lastly, the atomic positions and velocities must be provided. These are obtained by the SYSGEN routine, which reads the CONFIG file (section 4.1.2) and also generates the initial velocities if required to do so. If the system contains constraint bonds, the routine PASSCON is required to process molecular connectivity data and establish the communication procedure between nodes, and the QUENCH routine is required to set the starting velocities correctly. Also needed in the initialisation, is the routine FORGEN, which constructs the interpolation arrays for the short-range forces calculations, and the routine EXCLUDE which identifies atoms that are explictly chemically bonded through bonds, constraints or valence angles. The resulting list is known as the *excluded atoms* list.

The calculation of the pair forces represents the bulk of any simulation. A Verlet neighbour list is used by DL_POLY_2 in calculating the atomic forces. The routine that constructs this this is called PARLST. This routine builds the neighbour list taking into account the occurrence of atoms in the *excluded atoms* list. The routine SRFRCE calculates the short-range (van der Waals) forces, making use of the IMAGES routine to handle any periodic boundary conditions. Coulombic forces are handled by a varity of routines: COUL0, COUL1 and COUL2 handle Coulombic forces *without* periodic boundaries; EWALD1, EWALD2 and EWALD3 are used for systems *with* periodic boundaries (an additional routine: EWALD4 is necessary for the multiple timestep algorithm). Intramolecular forces require the routines ANGFRC, BNDFRC and DIHFRC. If the multiple timestep algorithm is required, the routine MULTIPLE must be used to call the various forces routines. It also calls the PRIMLST routine to split the interaction list into primary and secondary neighbours. The decision to update the neighbour list is handled by the routine VERTEST. The routine EXTNFLD is required if the simulated system has an external force field (e.g. electrostatic field) operating. To help with equilibration simulations, the routine FCAP is sometimes required to reduce the magnitude of badly equilibrated forces. Since DL_POLY_2 is based on the replicated data strategy, a global sum routine (GDSUM) is required to sum the atomic forces on all nodes.

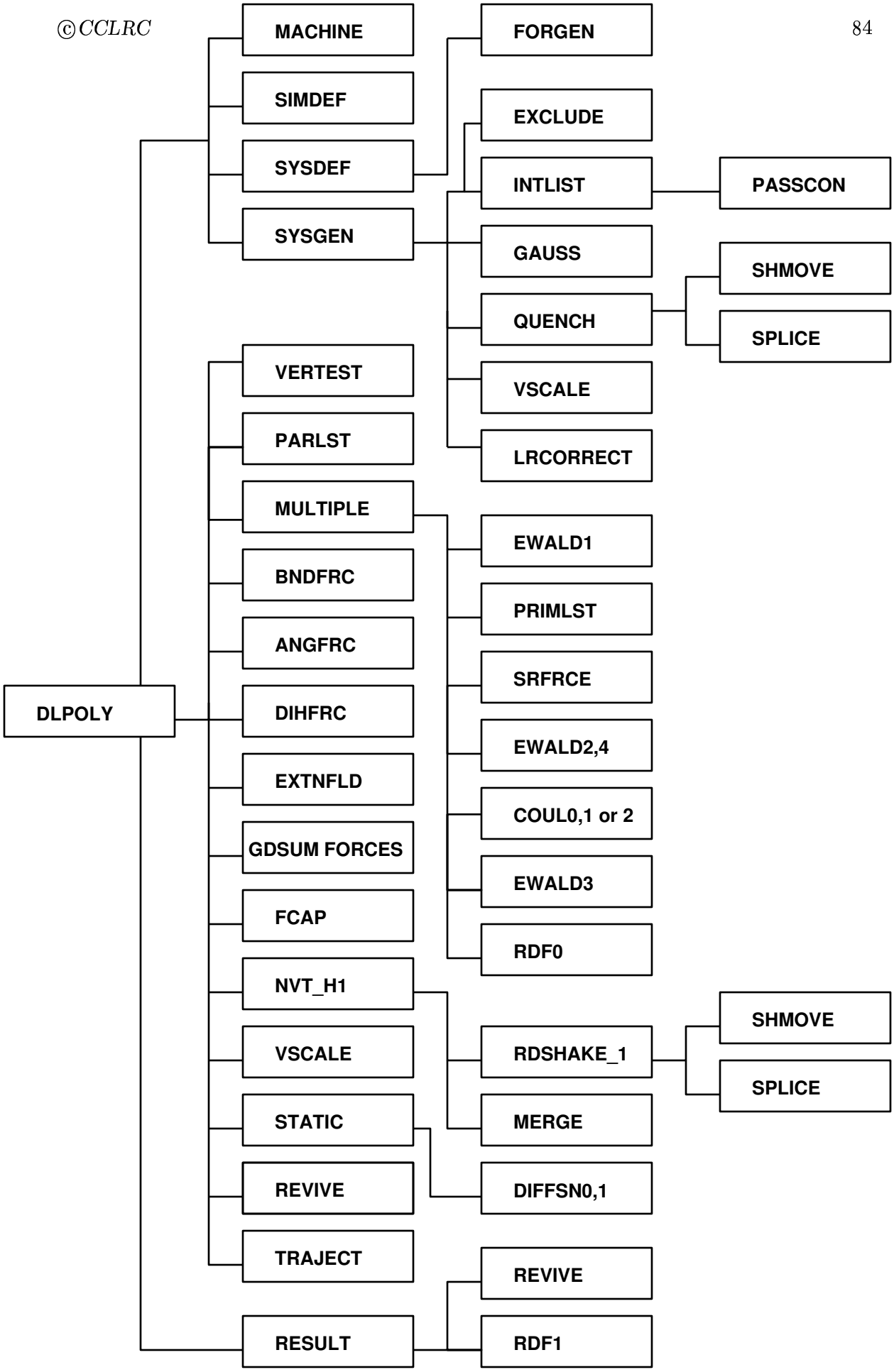
Integration of the equations of motion is handled by one of the routines listed and described in section 2.5. For example routines NVE_0, NVT_E0, NVT_H0, NVT_B0 etc. are used if no constraint forces are present. These routines treat the NVE, Evans-NVT, Hoover-Nosé-NVT and NVT-Berendsen ensembles respectively. The corresponding versions of these routines which handle constraint forces are NVE_1, NVT_E1, NVT_H1 or NVT_B1. These versions call the routine RDSHAKE_1 to handle the constraints. RDSHAKE_1 itself calls a number of additional routines: MERGE, SHMOVE and SPLICE. For *ad hoc* temperature scaling, the routine VSCALEG is required.

As mentioned elsewhere, DL_POLY_2 does not contain many routines for computing system properties during a simulation. Radial distributions may be calculated however, using the routines RDF0 and RDF1. Similarly DIFFSN0 and DIFFSN1 calculate approximate mean square displacements. Ordinary thermodynamic quantities are calculated by the routine STATIC, which also writes the STATIS file (section 4.2.7). Routine TRAJECT writes the HISTORY (section 4.2.1) file for later analysis.

Job termination is handled by the routine RESULT which writes the final summaries in the OUTPUT file and dumps the restart files REVIVE and REVCON (sections 4.2.4 and

4.2.3 respectively).

An idea of the construction of a DL_POLY_2 program can be obtained from the following flowchart. The example represents a DL_POLY_2 program which uses the multiple timestep algorithm, with bond constraints and the Nosé-Hoover thermostat.


DLPOLY
MACHINE
SIMDEF
SYSDEF
SYSGEN
FORGEN
EXCLUDE
INTLIST
PASSCON
GAUSS
SHMOVE
QUENCH
SPLICE
VSCALE
LRCORRECT
VERTEST
PARLST
MULTIPLE
EWALD1
BNDFRC
PRIMLST
ANGFRC
SRFRCE
DIHFRC
EWALD2,4
EXTNFLD
COUL0,1 or 2
GDSUM FORCES
EWALD3
FCAP
RDF0
NVT_H1
SHMOVE
VSCALE
RDSHAKE_1
SPLICE
STATIC
MERGE
REVIVE
DIFFSN0,1
TRAJECT
REVIVE
RESULT
RDF1

3.2 Compiling and Running DL_POLY_2

3.2.1 Compiling the Source Code

When you have obtained DL_POLY_2 from Daresbury Laboratory and unpacked it, your next task will be to compile it. To aid compilation a general makefile ("Makefile") has been provided in the sub-directory *build* (see Appendix A to this document). The general DL_POLY_2 makefile will build an executable with a wide range of functionality - sufficient for the test cases and for most users requirements. Other makefiles are found in the *build* sub-directory for variants of DL_POLY_2 , such as the respa version. Users will need to modify the makefile if they are to add additional functionality to the code, or if it requires adaptation for a non specified computer. Modifications may also be necessary if the Smooth Particle Mesh Ewald method is to be correctly incorporated (see below: "Modifying the makefile").

Copy the makefile from the *build* sub-directory to the *source* sub-directory and run it there - it will create the executable in the *execute* sub-directory. The compilation of the program is initiated by typing the command:

make target

where *target* is the specification of the required machine (e.g. sp2-mpi). For many computer systems this command is sufficient to compile a working version of DL_POLY_2 .

The full specification of the *make* command is as follows

make <TARGET= ... > < STRESS=... > < TYPE=... > < EX=... > < BINROOT=... > < PVM_NODES=... >

where some (or all) of the keywords may be omitted. The keywords and their use are described below. Note that keywords may also be set in the unix environment (e.g. with the "setenv" command in a C-shell).

The makefile first takes each FORTRAN routine in turn and scans it with a *C-preprocessor*. The purpose of this is to activate the required features in the code (and extract non-selected features from the original source code). For example if MPI is specified, all other message passing calls pertaining to PVM (for example) are removed. If NOSTRESS is specified, the statements for calculating the stress tensor are removed. The result of the preprocessing is a *temporary* FORTRAN file which is then compiled to produce the object code. If all is well, the makefile will combine the object code with the system libraries and produce the executable.

3.2.1.1 Keywords for the Makefile

1. **TARGET**

   The TARGET keyword indicates which kind of computer the code is to be compiled for. This **must** be specifed - there is no default value. Valid targets can be listed by the makefile if the command *make* is typed, without arguments. The list

frequently changes as more targets are added and redundant ones removed. Users are encouraged to extend the Makefile for themselves, using existing targets as examples.

2. **STRESS**

   The STRESS keyword activates the code that calculates the stress tensor in the DL_POLY_2 code. The arguments are:

   - NOSTRESS - if the stress tensor is not required;
   - STRESS - if the stress tensor is required (default).

   Calculation of the stress tensor is essential if "constant stress" (Rahman-Parrinello) MD is required.

3. **TYPE**

   The TYPE keyword creates variants of the DL_POLY_2 code which determine which scheme is to be used for the interpolation of the short-range potential and force arrays. The arguments are:

   - *3pt* - compile with 3-point interpolation (default);
   - *4pt* - compile with 4-point interpolation;
   - *rsq* - compile with r^2 interpolation.

   A discussion of the merits of the different interpolation methods is given below (section 3.2.1.3).

4. **EX**

   The EX keyword specifies the executable name. The default name for the executable is "DLPOLY.X".

5. **BINROOT**

   The BINROOT keyword specifies the directory in which the executable is to be stored. The default setting is "../execute".

6. **PVM_NODES**

   The PVM_NODES keywords specifies how many processes are to be invoked when the code is run under PVM. There is no default value. If this is not set at compile time the code will compile but produce an error message on execution. If you get this error (error 1) delete the module INITCOMMS.O and recompile with PVM_NODES set to a number consistent with a hypercube architecture (one of (1,) 2, 4, 8 etc).

3.2.1.2 Modifying the Makefile

1. **Changing the TARGET**

   If you do not intend to run DL_POLY_2 on one of the specified machines, you must add appropriate lines to the makefile to suit your circumstances. The safest way to do this is to modify an existing TARGET option for your purposes. The makefile supplied with DL_POLY_2 contains examples for serial, PVM, and MPI environments as well as for Intel and Cray (T3E) parallel machines so you should find one close to your requirements. You must of course be familiar with the appropriate invocation of the FORTRAN compiler for your local machine and also any alternatives to PVM or MPI your local machine may be running. After DL_POLY_2 Version 2.12, the required C preprocessor is supplied with the source code, and is called dpp.c (written by J. Genornowicz, Southampton University, 1999). If you wish to compile for MPI or PVM systems remember to ensure the appropriate library directories are included in the C-preprocessing flags (CPPFLAGS). If you intend the program for a single processor machine use the flag -DSERIAL (see the "sun" example in the makefile).

2. **Enabling the Smooth Particle Mesh Ewald**

   Users of DL_POLY_2 Version 2.12 (and above) should note that modifications to the makefile may be required if the code is automatically to incorporate the Smooth Particle Mesh Ewald (SPME) . Primarily this requires a specification of the system library location of the 3D Fast Fourier Transform (FFT) routine implicit in the method. The default FFT routine for DL_POLY_2 is the public domain code FFTW, but this is not specified for all platforms represented in the makefile. The user who wishes to use the SPME feature should check the relevant part of the makefile to make sure this is enabled (this is generally made clear in the makefile comments). The SPME feature is enabled by setting the parameter FFTW_LIBRARY to specify the location of the FFTW software, and by inserting the flag -DFFTW in the CPFLAGS list (see above). Note that for most parallel systems represented in the makefile the appropriate FFT is already enabled (which is usually not FFTW). This is particularly the case for Cray T3E, IBM SP/2 and parallel SGI machines.

3. **MPI and PVM implementations**

   The implementation of MPI may differ between sites. On some systems the Fortran callable subroutine names are expected to end with an underscore ("_"). If this is the case the flag -DMPIU must be included as part of the C-preprocessing flags and the file "mpif.h" copied from the MPI library directory into the *source* directory. Alternatively you can set the path to the MPI library either the "-I" option on the C-preprocessing flags. The DL_POLY_2 makefile assumes you have copied the file over (see the entry *hp-mpi:* in the makefile). This appends an underscore to all MPI subroutine names and to the name of the MPI common block. If the underscores are not required the flag must be omitted (see the entry "*sp2-mpi:*).

When using MPI you need a copy of the MPI include file "mpif.h" in the source directory. On many machines this is stored in the /usr/include directory, in which case the make procedure should find it automatically (as it also does for IBM SP/2 and Cray T3E machines, where it is stored elsewhere). However, if the make reports a failure to find the "mpif.h" file, you must amend the makefile to ensure that it copied from the true location before C-preprocessing is attempted. There are several examples in the makefile of how this is done.

Similarly when using PVM you need to place a copy of the PVM include file "pvmf.h" in the source directory or copy it in before C-preprocessing.

4. **Problems with optimization ?**

   Some subroutines do not compile correctly when using optimization on some compilers. This is not the fault of the DL_POLY_2 code, but of the compiler concerned. This is circumvented by compiling the offending subroutines unoptimised. See the entries for various machines in the makefile to see how this is done if you experience problems with other subroutines.

5. **Changing the Timer**

   The only other routine likely to cause problems is TIMCHK, which requires a machine specific timer. The makefile should select the appropriate timer for you, but if the timer routine you require is not included you will need to add the appropriate lines of code. TIMCHK returns the elapsed time in seconds. Note that the C routine ETIME may be used on many unix systems. It is used as the default timer by DL_POLY_2 on serial and PVM systems.

6. **Adding new functionality**

   To include a new subroutine in the code simply add *subroutine*.o to the list of object names in the makefile. The simpliest way is to add names to the "OBJ_ALL" list.

3.2.1.3 Note on Interpolation Schemes

In DL_POLY_2 the short-range (Van der Waals) contributions to energy and force are evaluated by interpolation of tables constructed at the beginning of execution. DL_POLY_2 caters for three different interpolation schemes: 3-point and 4-point in r-space and linear interpolation in r^2-space. Tabulation in r^2 avoids the use of the square root function in evaluation of the non-bonded interactions, and thus typically decreases execution time by 10-15 %. Note that tabulation in r^2 usually requires more grid points (and hence more memory) than tabulation in r. This is to ensure sufficient accuracy is retained at small r.

A guide to the *minimum* number of grid points (`mxgrid`) required for interpolation in r to give good energy conservation in a simulation is:

$$\texttt{mxgrid} \geq 100(\texttt{rcut}/\texttt{rmin})$$

where `rmin` is the *smallest* position minimum of the non-bonded potentials in the system. The parameter `mxgrid` is defined in the DL_PARAMS.INC file, and must be set before compilation.

A guide to the *minimum* number of grid points required for interpolation in r^2 is:

$$\texttt{mxgrid} \geq 100(\texttt{rcut}/\texttt{rmin})^2$$

where `rmin` is again the smallest position minimum of the non-bonded potentials in the system.

For users in doubt as whether to use r or r^2-space interpolation we recommend the former. This is because tabulation in r is less demanding on memory requirements and less prone to inaccuracy should too small a value of `mxgrid`, or too large a value of `rcut`, be used. Tabulation in r is therefore the default option for DL_POLY, r^2 interpolation can be specified at compile time by 'making' the executable with the directive **TYPE=rsq**.

The other issue of concern to users is the choice of 3 or 4 point schemes in r-space interpolation. The relative merits are as follows: 4 point interpolation may permit a smaller number of grid points to be used in the interpolation tables thus saving on memory requirements. 3 point interpolation is quicker than 4 point interpolation and normally sufficiently accurate. The choice involves decisions about speed, accuracy and memory requirements. 3-point interpolation is the default option.

A utility program TABCHK is provided in the DL_POLY *utility* sub-directory to help users choose a sufficiently accurate interpolation scheme (including array sizes) for their needs.

3.2.2 Assisting Compilation with the Utility Program PARSET

A particular difficulty in creating a working version of DL_POLY_2 **prior** to version 2.11 is creating the DL_PARAMS.INC file (section 7.1.1), which specifies (among other things) the array sizes for the compiled code. The copy of DL_PARAMS.INC supplied with DL_POLY_2 contains settings appropriate for the test cases and some of the benchmarks but is not guaranteed to be appropriate for any user's specific requirements. Users must determine their own requirements and so produce their own version of DL_PARAMS.INC before compiling a working version. While DL_POLY_2 contains many error checks to prevent the arrays being exceeded during a run, it is tedious to have to recompile the code each time an error is detected. Furthermore the large number of parameters required to specify the entire code makes it very unlikely that the code will run successfully first time, or even after several attempts.

To assist with this difficulty, the utility program PARSET has been created (section 6.1.1). It can be used to create a DL_PARAMS.INC file that is suitable for the simulation being attempted. It works by scanning the DL_POLY_2 input files (CONTROL, FIELD and CONFIG) and then writing out a sample DL_PARAMS.INC file, which has the name NEW_PARAMS.INC.

PARSET is not foolproof however. The user must prepare the correct input files beforehand, which can be difficult without the error checking the DL_POLY_2 code affords. Also, because of the complexity of the requirements, PARSET can only supply a reasonable

estimate of some of the array dimensions, and these may not be quite right for every case. (It will be reasonably close however). Notwithstanding the limitations of PARSET its use as a labour saving device is recommended.

PARSET is described in detail in section 6.1.1. The program is found in the *utility* subdirectory.

3.2.3 Running DL_POLY_2

To run the DL_POLY_2 executable (DLPOLY.X) you will initially require three, possibly four, input data files, which you must create in the *execute* sub-directory, (or whichever sub-directory you keep the executable program.) The first of these is the CONTROL file (section 4.1.1), which indicates to DL_POLY_2 what kind of simulation you want to run, how much data you want to gather and for how long you want the job to run. The second file you need is the CONFIG file (section 4.1.2). This contains the atom positions and, depending on how the file was created (e.g. whether this is a configuration created from 'scratch' or the end point of another run), the velocities also. The third file required is the FIELD file (section 4.1.3), which specifies the nature of the intermolecular interactions, the molecular topology and the atomic properties, such as charge and mass. Sometimes you will require a fourth file: TABLE (section 4.1.5), which contains the potential and force arrays for functional forms not available within DL_POLY_2 (usually because they are too complex e.g. spline potentials).

Examples of input files are found in the *data* sub-directory, which can be copied into the *execute* subdirectory using the *select* macro found in the *execute* sub-directory.

A successful run of DL_POLY_2 will generate several data files, which appear in the *execute* sub-directory. The most obvious one is the file OUTPUT (section 4.2.2), which provides an effective summary of the job run: the input information; starting configuration; instantaneous and rolling-averaged thermodynamic data; final configurations; radial distribution functions (RDFs); and job timing data. The OUTPUT file is human readable. Also present will be the restart files REVIVE (section 4.2.4) and REVCON (section 4.2.3). REVIVE contains the accumulated data for a number of thermodynamic quantities and RDFs, and is intended to be used as the input file for a following run. It is *not* human readable. The REVCON file contains the *restart configuration* i.e. the final positions, velocities and forces of the atoms when the run ended and is human readable. The STATIS file (section 4.2.7) contains a catalogue of instantaneous values of thermodynamic and other variables, in a form suitable for temporal or statistical analysis. Finally, the HISTORY file (section 4.2.1) provides a time ordered sequence of configurations to facilitate further analysis of the atomic motions. Depending on which version of the TRAJECT subroutine you compiled in the code, this file may be either formatted (human readable) or unformatted. You may move these output files back into the *data* sub-directory using the *store* macro found in the *execute* sub-directory.

Note that versions of DL_POLY_2 after 2.10 may also create the files RDFDAT and ZDNDAT, containing the RDF and Z-density data respectively. They are both human readable files.

3.2.4 Restarting DL_POLY_2

The best approach to running DL_POLY_2 is to define from the outset precisely the simulation you wish to perform and create the input files specific to this requirement. The program will then perform the requested simulation, but may terminate prematurely through error, inadequate time allocation or computer failure. Errors in input data are your responsibility, but DL_POLY_2 will usually give diagnostic messages to help you sort out the trouble. Running out of job time is common and provided you have correctly specified the job time variables (using the **close time** and **job time** directives - see section 4.1.1) in the CONTROL file, DL_POLY_2 will stop in a controlled manner, allowing you to restart the job as if it had not been interrupted.

To restart a simulation after normal termination you will again require the CONTROL file, the FIELD (and TABLE) file, and a CONFIG file, which is the exact copy of the REVCON file created by the previous job. You will also require a new file: REVOLD (section 4.1.4), which is an exact copy of the previous REVIVE file. If you attempt to restart DL_POLY_2 without this additional file available, the job will fail. Note that DL_POLY_2 will append new data to the existing STATIS and HISTORY files if the run is restarted, other output files will be **overwritten**.

In the event of machine failure, you should be able to restart the job in the same way from the surviving REVCON and REVIVE files, which are dumped at intervals to meet just such an emergency. In this case check carefully that the input files are intact and use the HISTORY and STATIS files with caution - there may be duplicated or missing records. The reprieve processing capabilities of DL_POLY_2 are not foolproof - the job may crash while these files are being written for example, but they can help a great deal. You are advised to keep backup copies of these files, noting the times they were written, to help you avoid going right back to the start of a simulation.

You can also extend a simulation beyond its initial allocation of timesteps, provided you still have the REVCON and REVIVE files. These should be copied to the CONFIG and REVOLD files respectively and the directive **timesteps** adjusted in the CONTROL file to the new total number of steps required for the simulation. For example if you wish to extend a 10000 step simulation by a further 5000 steps use the directive **timesteps 15000** in the CONTROL file and include the **restart** directive. You can use the **restart scale** directive if you want to reset the temperature at the restart, but note that this also resets all internal accumulators (timestep included) to zero.

3.3 A Guide to Preparing Input Files

The CONFIG file and the FIELD file can be quite large and unwieldy particularly if a polymer or biological molecule is involved in the simulation. This section outlines the paths to follow when trying to construct files for such systems. The description of the DL_POLY_2 force field in chapter 2 is essential reading. The various utility routines mentioned in this section are described in greater detail in chapter 6. Many of these have been incorporated into the DL_POLY_2 Graphical User Interface [20] and may be convenently used from there.

3.3.1 Inorganic Materials

The utility GENLAT can be used to construct the CONFIG file for relatively simple lattice structures. Input is interactive. The FIELD file for such systems are normally small and can be constructed by hand. The utility GENLAT.TO constructs the CONFIG file for truncated-octahedral boundary conditions. Otherwise the input of force field data for crystalline systems is particularly simple, if no angular forces are required (notable exceptions to this are zeolites and silicate glasses - see below). Such systems require only the specification of the atomic types and the necessary pair forces. The reader is referred to the description of the DL_POLY_2 FIELD file for further details (section 4.1.3).

DL_POLY_2 allows the simulation of zeolites and silicate (or other) glasses. Both these materials require the use of angular forces to describe the local structure correctly. In both cases the angular terms are included as *three body terms*, the forms of which are described in chapter 2. These terms are entered into the FIELD file with the pair potentials. Note that you cannot use truncated octahedral or rhombic dodecahedral boundary conditions in conjunction with three body forces, due to the use of the link-cell algorithm for evaluating the forces.

An alternative way of handling zeolites is to treat the zeolite framework as a kind of macromolecule (see below). This was the suggested method for users of DL_POLY_1.1, and experience showed that this is quite adequate, provided it is remembered that the periodicity of the system requires that "bonds" be described that cross the boundaries of the MD cell and link with images of atoms from the opposite side. Specifying all this is tedious and is best done computationally: what is required is to determine the nearest image neighbours of all atoms and assign appropriate bond and valence angle potentials. (This may require the definition of new bond forces in subroutine BNDFRC, but this is easy.) What must be avoided at all costs is specifying the angle potentials *without* specifying bond potentials. In this case DL_POLY_2 will automatically cancel the non-bonded forces between atoms linked via valence angles and the system will collapse. The advantage of this method is that the calculation is likely to be faster using three-body forces. This method is not recommended for amorphous systems.

3.3.2 Macromolecules

Simulations of proteins are best tackled using the package DLPROTEIN [21] which is an adaptation of DL_POLY specific to protein modelling. However you may simulate proteins and other macromolecules with DL_POLY_2 if you wish. This is described below.

If you select a *protein* structure from a SEQNET file (e.g. from the Brookhaven database), use the utility PROSEQ to generate the file CONFIG. This will then function as input for DL_POLY_2 . Some caution is required here however, as the protein structure may not be fully determined and atoms may be missing from the CONFIG file.

If you have the "edit.out" file produced by AMBER for your molecule use this as the CONNECT_DAT input file for the utility AMBFORCE. AMBFORCE will produce the DL_POLY_2 FIELD and CONFIG files for your molecule.

If you do not have the "edit.out" file things are a little more tricky, particularly in

coming up with appropriate partial charges for atomic sites. However there are a series of utilities that will at least produce the CONNECT_DAT file for use with AMBFORCE. We now outline these utilities and the order in which they should be used.

If you have a structure from the Cambridge Structural database (CSDB) then use the utility FRACCON to take fractional coordinate data and produce a CONNECT_DAT and "ambforce.dat" file for use with AMBFORCE. Note that you will need to modify FRACCON to get the AMBER names correct for sites in your molecule. The version of FRACCON supplied with DL_POLY_2 is specific to the valinomycin molecule.

If you require an all atom force field and the database file does not contain hydrogen positions then use the utility FRACFILL in place of FRACCON. FRACCON produces an output file HFILL which should then be used as input for the utility HFILL. The HFILL utility fills out the structure with the missing hydrogens. (Note that you may need to know what the atomic charges are in some systems, for example the AMBER charges from the literature.)

Note: with minor modifications the utilities FRACFILL and FRACCON can be used on structures from databases other than the Cambridge structural database.

3.3.3 Adding Solvent to a Structure

The utility WATERADD adds water from an equilibrated configuration of 256 SPC water molecules at 300 K to fill out the MD cell. The utility SOLVADD fills out the MD box with single-site solvent molecules from a f.c.c lattice. The FIELD files will then need to be edited to account for the solvent molecules added to the file.

Hint: to save yourself some work in entering the non-bonded interactions variables involving solvent sites to the FIELD file put two bogus atoms of each solvent type at the end of the CONNECT_DAT file (for AMBER force-fields) the utility AMBFORCE will then evaluate all the non-bonded variables required by DL_POLY_2 . Remember to delete the bogus entries from the CONFIG file before running DL_POLY_2 .

3.3.4 Analysing Results

DL_POLY_2 is not designed to calculate every conceivable property you might wish from a simulation. Apart from some obvious thermodynamic quantities and radial distribution functions, it does not calculate anything beyond the atomic trajectories on-line. You must therefore be prepared to post-process the HISTORY file if you want other information. There are some utilities in the DL_POLY_2 package to help with this, but the list is far from exhaustive. In time, we hope to have many more. Our users are invited to submit code to the DL_POLY_2 *public* library to help with this.

The utilities available are described in the DL_POLY_2 Reference Manual 6. Users should also be aware that many of these utilities are incorporated into the DL_POLY_2 Graphical User Interface [20].

3.3.5 Choosing Ewald Sum Variables

This section outlines how to optimise the accuracy of the Ewald sum parameters for a given simulation. In what follows the directive **spme** may be used anywhere in place of the

directive **ewald** if the user wishes to use the Smooth Particle Mesh Ewald method.

As a guide to beginners DL_POLY_2 will calculate reasonable parameters if the **ewald precision** directive is used in the CONTROL file (see section 4.1.1). A relative error (see below) of 10^{-6} is normally sufficient so the directive

ewald precision 1d-6

will cause DL_POLY_2 to evaluate its best guess at the Ewald parameters α, `kmax1`, `kmax2` and `kmax3`. (The user should note that this represents an *estimate*, and there are sometimes circumstances where the estimate can be improved upon. This is especially the case when the system contains a strong directional anisotropy, such as a surface.) These four parameters may also be set explicitly by the **ewald sum** directive in the CONTROL file. For example the directive

ewald sum 0.35 6 6 8

would set $\alpha = 0.35$ Å^{-1}, `kmax1` $= 6$, `kmax2 = 6` and `kmax3` $= 8$. The quickest check on the accuracy of the Ewald sum is to compare the Coulombic energy (U) and the coulombic virial ($\mathcal{W}$) in a short simulation. Adherence to the relationship $U = -\mathcal{W}$ shows the extent to which the Ewald sum is correctly converged. These variables can be found under the columns headed `eng_cou` and `vir_cou` in the OUTPUT file (see section 4.2.2).

The remainder of this section explains the meanings of these parameters and how they can be chosen. The Ewald sum can only be used in a three dimensional periodic system. There are three variables that control the accuracy: α, the Ewald convergence parameter; $r_{\rm cut}$ the real space forces cutoff; and the `kmax1,2,3` integers [1] that effectively define the range of the reciprocal space sum (one integer for each of the three axis directions). These variables are not independent, and it is usual to regard one of them as pre-determined and adjust the other two accordingly. In this treatment we assume that $r_{\rm cut}$ (defined by the **cutoff** directive in the CONTROL file) is fixed for the given system.

The Ewald sum splits the (electrostatic) sum for the infinite, periodic, system into a damped real space sum and a reciprocal space sum. The rate of convergence of both sums is governed by α. Evaluation of the real space sum is truncated at $r = r_{\rm cut}$ so it is important that α be chosen so that contributions to the real space sum are negligible for terms with $r > r_{\rm cut}$. The relative error (ϵ) in the real space sum truncated at $r_{\rm cut}$ is given approximately by

$$\epsilon \approx {\rm erfc}(\alpha r_{\rm cut})/r_{\rm cut} \approx \exp[-(\alpha.r_{\rm cut})^2]/r_{\rm cut} \tag{3.1}$$

The recommended value for α is $3.2/r_{\rm cut}$ or greater (too large a value will make the reciprocal space sum very slowly convergent). This gives a relative error in the energy of no greater than $\epsilon = 4 \times 10^{-5}$ in the real space sum. When using the directive **ewald precision** DL_POLY_2 makes use of more sophisticated approximation:

$${\rm erfc}(x) \approx 0.56 \exp(-x^2)/x \tag{3.2}$$

[1] **Important note:** For the SPME method the values of `kmax1,2,3` should be double those obtained in this prescription, since they specify a cubic lattice, not a radius of convergence.

to solve recursively for α, using equation 3.1 to give the first guess.

The relative error in the reciprocal space term is approximately

$$\epsilon \approx \exp(-k_{max}^2/4\alpha^2)/k_{max}^2 \tag{3.3}$$

where

$$k_{max} = \frac{2\pi}{L}\ \texttt{kmax} \tag{3.4}$$

is the largest k-vector considered in reciprocal space, L is the width of the cell in the specified direction and `kmax` is an integer.

For a relative error of 4×10^{-5} this means using $k_{max} \approx 6.2\alpha$. `kmax` is then

$$\texttt{kmax} > 3.2\ L/r_{\rm cut} \tag{3.5}$$

In a cubic system, $r_{\rm cut} = L/2$ implies `kmax` $= 7$. In practice the above equation slightly over estimates the value of `kmax` required, so optimal values need to be found experimentally. In the above example `kmax` $= 5$ or 6 would be adequate.

If your simulation cell is a truncated octahedron or a rhombic dodecahedron then the estimates for the `kmax` need to be multiplied by $2^{1/3}$. This arises because twice the normal number of k-vectors are required (half of which are redundant by symmetry) for these boundary contributions [30].

If you wish to set the Ewald parameters manually (via the **ewald sum** or *spme sum* directives) the recommended approach is as follows. Preselect the value of $r_{\rm cut}$, choose a working a value of α of about $3.2/r_{\rm cut}$ and a large value for the `kmax` (say 10 10 10 or more). Then do a series of ten or so *single* step simulations with your initial configuration and with α ranging over the value you have chosen plus and minus 20%. Plot the Coulombic energy (and $-\mathcal{W}$) versus α. If the Ewald sum is correctly converged you will see a plateau in the plot. Divergence from the plateau at small α is due to non-convergence in the real space sum. Divergence form the plateau at large α is due to non-convergence of the reciprocal space sum. Redo the series of calculations using smaller `kmax` values. The optimum values for `kmax` are the smallest values that reproduce the correct Coulombic energy (the plateau value) and virial at the value of α to be used in the simulation.

Note that one needs to specify the three integers (`kmax1, kmax2, kmax3`) referring to the three spatial directions, to ensure the reciprocal space sum is equally accurate in all directions. The values of `kmax1`, `kmax2` and `kmax3` must be commensurate with the cell geometry to ensure the same minimum wavelength is used in all directions. For a cubic cell set `kmax1` = `kmax2` = `kmax3`. However, for example, in a cell with dimensions $2A = 2B = C$ (ie. a tetragonal cell, longer in the c direction than the a and b directions) use 2`kmax1` = 2`kmax2` = (`kmax3`).

If the values for the `kmax` used are too small, the Ewald sum will produce spurious results. If values that are too large are used, the results will be correct but the calculation will consume unnecessary amounts of *cpu* time. The amount of *cpu* time increases with `kmax1` × `kmax2` × `kmax3`.

3.4 DL_POLY_2 Error Processing

3.4.1 The DL_POLY_2 Internal Error Facility

DL_POLY_2 contains a number of in-built error checks scattered throughout the package which detect a wide range of possible errors. In all cases, when an error is detected the subroutine ERROR is called, resulting in an appropriate message and termination of the program execution (either immediately, or after additional processing.).

Users intending to insert new error checks should ensure that all error checks are performed *concurrently* on *all* nodes, and that in circumstances where a different result may obtain on different nodes, a call to the global status routine GSTATE is made to set the appropriate global error flag on all nodes. Only after this is done, a call to subroutine ERROR may be made. An example of such a procedure might be:

```
logical safe
safe=(test_condition)
call gstate(safe)
if(.not.safe) call error(node_id,message_number)
```

In this example it is assumed that the logical operation *test_condition* will result in the answer *.true.* if it is safe for the program to proceed, and *.false.* otherwise. The call to ERROR requires the user to state the identity of the calling node (`node_id`), so that only the nominated node in ERROR (i.e. node 0) will print the error message. The variable `message_number` is an integer used to identify the appropriate message to be printed.

In all cases, if ERROR is called with a *non-negative* message number, the program run terminates. If the message number is *negative*, execution continues, but even in this case DL_POLY_2 will terminate the job at a more appropriate place. This feature is used in processing the CONTROL and FIELD file directives. A possible modification users may consider is to dump additional data before the call to ERROR is made.

A description of the ERROR subroutine is found in chapter 7 the DL_POLY_2 Reference Manual.

A full list of the DL_POLY_2 error messages and the appropriate user action can be found in Appendix C of this document.

Chapter 4

DL_POLY_2 Data Files

Scope of Chapter

This chapter describes all the input and output files for DL_POLY_2 , examples of which are to be found in the *data* sub-directory.

4.1 The INPUT files

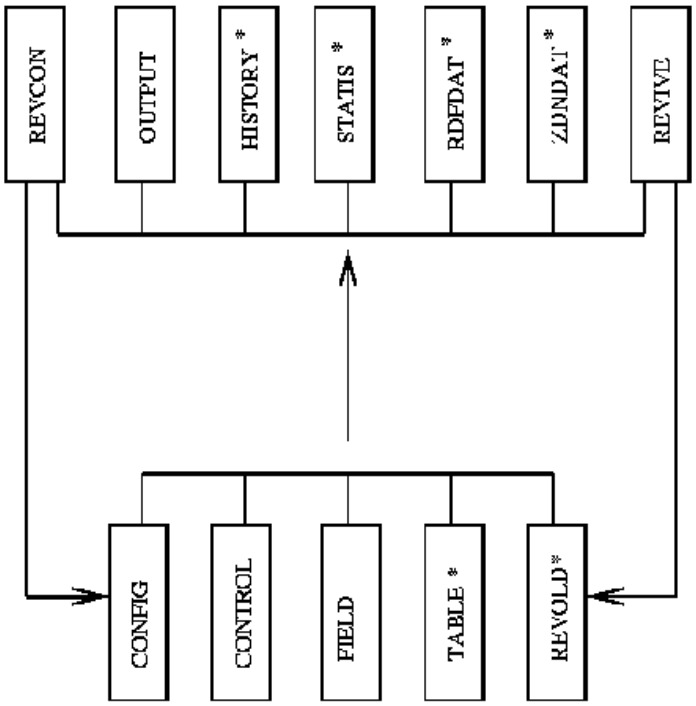


Figure 4.1: DL_POLY_2 input (left) and output (right) files. Note: files marked with an asterisk are non-mandatory.

DL_POLY_2 requires five input files named CONTROL, CONFIG, FIELD, TABLE and REVOLD. The first three files are mandatory, while TABLE is used only to input certain kinds of pair potential, and is not always required. REVOLD is required only if the job represents a continuation of a previous job. In the following sections we describe the form and content of these files.

4.1.1 The CONTROL File

The CONTROL file is read by the subroutine SIMDEF and defines the control variables for running a DL_POLY_2 job. It makes extensive use of **directives** and **keywords**. Directives are character strings that appear as the first entry on a data record (or line) and which invoke a particular operation or provide numerical parameters. Also associated with each directive may be one or more keywords, which may qualify a particular directive by, for example, adding extra options. Directives can appear in any order in the CONTROL file, except for the **finish** directive which marks the end of the file. Some of the directives

are mandatory (for example the **timestep** directive that defines the timestep), others are optional.

This way of constructing the file is very convenient, but it has inherent dangers. It is, for example, quite easy to specify the same directive more than once, or specify contradictory directives, or invoke algorithms that do not work together. By and large DL_POLY_2 tries to sort out these difficulties and print helpful error messages, but it does not claim to be foolproof. Fortunately in most cases the CONTROL file will be small and easy to check visually. It is important to think carefully about a simulation beforehand and ensure that DL_POLY_2 is being asked to do something that is physically reasonable. It should also be remembered that the present capabilites the package may not allow the simulation required and it may be necessary for you yourself to add new features.

An example CONTROL file appears below. The directives and keywords appearing are described in the following section.

```
Title Record: Example CONTROL file for DL_POLY

# define the state point
temperature             300.0

# simulation length and equilibration
steps                    2000
equilibration steps      1000
scale every                 5 steps
timestep                0.0005 ps
multiple timestep           1 steps

# specify cutoffs
cutoff                    7.6 angstrom
delr                      0.5 angstrom

# print controller
print every               100 steps

# rdf options
rdf sampling every         10 steps
print rdf

# job time and permitted wind-up time
job time                21000 seconds
close time                200 seconds

# forces options
ewald sum          0.48 6 6 6
cap forces in equilibration mode 2000 kT/A
```

```
# ensemble options
ensemble   nve (default option)

# statistics controls
stats every              2000 steps
stack                     100 deep

# trajectory dumping controls
trajectory nstraj 1 istraj 50  keytrj 0

finish
```

4.1.1.1 The CONTROL file format

The file is free-formatted, integers, reals and additional keywords are entered following the directive on each record. Real and integer numbers must be separated by a non-numeric character (preferably a space or comma) to be correctly interpreted. No logical variables appear in the control file. Comment records (beginning with a #) and blank lines may be added to aid legibility (see example above). Additional annotation may be added onto the directive line, provided it does not contain numerical characters, or appear where a directive or keyword is expected. The CONTROL file is not case sensitive.

- The first record in the CONTROL file is a header 80 characters long, to aid identification of the file.
- The last record is a **finish** directive, which marks the end of the input data.

Between the header and the **finish** directive, a wide choice of control directives may be inserted. These are described below.

4.1.1.2 The CONTROL File Directives

The directives available are as follows.

directive:	**meaning:**
all pairs	use all pairs for electrostatic calculations
cap *f*	cap forces during equilibration period *f* is maximum cap in units of kT/Å (default *f*=1000)
close time *f*	set job closure time to *f* seconds
collect	include equilibration data in overall statistics
coul	calculate coulombic forces
cut *f*	set required forces cutoff to *f* (Å)

distan calculate coulombic forces using distance dependent dielectric

delr *f* set Verlet neighbour list shell width to *f* (Å)

ensemble nve select NVE ensemble (default)

ensemble nvt ber *f*
select NVT ensemble with Berendsen thermostat
with relaxation constant *f* (ps)

ensemble nvt evans
select NVT ensemble with Evans thermostat

ensemble nvt hoover *f*
select NVT ensemble with Hoover-Nose thermostat
with relaxation constant *f* (ps)

ensemble npt ber f_1 f_2
select Berendsen NPT ensemble with f_1, f_2
as the thermostat and barostat relaxation times (ps)

ensemble npt hoover f_1 f_2
select Hoover NPT ensemble with f_1, f_2
as the thermostat and barostat relaxation times (ps)

ensemble nst ber f_1 f_2
select Berendsen N$\underline{\underline{\sigma}}$T ensemble, with f_1, f_2
as the thermostat and barostat relaxation times (ps)

ensemble nst hoover f_1 f_2
select Hoover N$\underline{\underline{\sigma}}$T ensemble with f_1, f_2
as the thermostat and barostat relaxation times (ps)

ensemble pmf select (NVE) potential of mean force ensemble

eps *f* set relative dielectric constant to *f* (default 1.0)

equil *n* equilibrate simulation for first *n* timesteps

ewald precision *f* select Ewald sum for electrostatics, with
automatic parameter optimisation ($0 < f < .5$)

ewald sum α *k1 k2 k3*
select Ewald sum for electrostatics, with:
α = Ewald convergence parameter (Å^{-1})
k1 = maximum k-vector index in x-direction
k2 = maximum k-vector index in y-direction
k3 = maximum k-vector index in z-direction

finish close the CONTROL file (last data record)

job time *f* set job time to *f* seconds

mult *n* set multiple timestep (multi-step)interval (activated when n>2)

no elec ignore coulombic interactions

no vdw ignore short range (non-bonded) interactions

pres *f* set required system pressure to *f* k.bars
(target pressure for constant pressure ensembles)

prim *f* set primary cutoff to *f* (Å)
(for multiple timestep algorithm only)

print *n*	print system data every *n* timesteps
print rdf	print radial distribution functions
quaternion *f*	set quaternion tolerance to *f* (default 10^{-8})
rdf *f*	calculate radial distribution functions at intervals of *f* timesteps
reaction	select reaction field electrostatics
restart	restart job from end point of previous run (i.e. continue current simulation)
restart scale	restart job from previous run with temperature scaling (i.e. begin a new simulation from older run)
scale *n*	rescale atomic velocities every *n* steps (during equilibration)
shake *f*	set shake tolerance to *f* (default 10^{-8})
shift	calculate electrostatic forces using shifted coulombic potential
spme precision *f*	select Ewald sum for electrostatics, with automatic parameter optimisation ($0 < f < .5$)
spme sum α *k1 k2 k3*	select Ewald sum for electrostatics, with: α = Ewald convergence parameter (Å^{-1}) *k1* = maximum k-vector index in x-direction *k2* = maximum k-vector index in y-direction *k3* = maximum k-vector index in z-direction
stack *n*	set rolling average stack to *n* timesteps
stats *n*	accumulate statistics data every *n* timesteps
steps *n*	run simulation for *n* timesteps
temp *f*	set required simulation temperature to *f* K
traj *i j k*	write HISTORY file with controls: *i* = start timestep for dumping configurations *j* = timestep interval between configurations *k* = data level (i.e. variable `keytrj` see table 4.3)
timestep *f*	set timestep to *f* ps
zden	calculate the z-density profile
zero	perform zero temperature MD run

4.1.1.3 Further Comments on the CONTROL File

1. A number of the directives (or their **mutually exclusive** alternatives) are **mandatory**:
   (a) **timestep**: specifying the simulation timestep;
   (b) **temp** or **zero** : specifying the system temperature (not mutually exclusive);
   (c) **ewald sum** or **ewald precision** or **coul** or **shift** or **distan** or **reaction** or **no elec**: specifying the required coulombic forces option;
   (d) **cut** and **delr**: specifying the short range forces cutoff and Verlet strip;

(e) **prim**: specifying primary forces cutoff (**if mult>2 only**).

2. The **job time** and **close time** directives are required to ensure a controlled close down procedure when a job runs out of time. The time specified by the **job time** directive indicates the total time allowed for the job. (This must obviously be set equal to the time specified to the operating system when the job is submitted.) The **close time** directive represents the time DL_POLY_2 will require to write and close all the data files at the end of processing. This means the *effective* processing time limit is equal to the job time minus the close time. Thus when DL_POLY_2 reaches the effective job time limit it begins the close down procedure with enough time in hand to ensure the files are correctly written. In this way you may be sure the restart files etc. are complete when the job terminates. Note that setting the close time too small will mean the job will crash before the files have been finished. If it is set too large DL_POLY_2 will begin closing down too early. How large the close time needs to be to ensure safe close down is system dependent and a matter of experience. It generally increases with the job size.

3. The starting options for a simulation are governed by the keyword **restart**. If this is **not** specified in the CONTROL file, the simulation will start as new. If specifed, it will either continue a previous simulation (**restart**) or start a new simulation with initial temperature scaling of the previous configuration (**restart scale**). Internally these options are handled by the integer variable `keyres`, which is explained in table 4.1.

4. The various **ensemble** options (i.e. **nve**, **nvt ber**, **nvt evans, nvt hoover, npt ber, npt hoover**, **nst ber**, **nst hoover**) are mutually exclusive, though none is mandatory (the default is the NVE ensemble). These options are handled internally by the integer variable `keyens`. The meaning of this variable is explained in table 4.2.

5. The force selection directives **ewald sum**, **ewald precision**, **reaction**, **coul**, **shift**, **dist**, **no elec** and **no vdw** are handled internally by the integer variable `keyfce`. See table 4.4 for an explanation of this variable. Note that these options are mutually exclusive.

6. The choice of reaction field electrostatics (directive **reaction**) requires also the specification of the relative dielectric constant external to the cavity. This is specified in the **eps** directive.

7. DL_POLY_2 uses as many as three different potential cutoffs. These are as follows:

   (a) `rcut` - this is the universal cutoff. It applies to the real space part of the electrostatics calculations and to the van der Waals potentials if no other cutoff is applied;

   (b) `rvdw` - this is the user-specified cutoff for the van der Waals potentials. If not specified its value defaults to `rcut`;

(c) `rprim` - this is used in the multiple timestep algorithm to specify the primary atom region (see section 2.5.7). It has no meaning if the multiple timestep option is not used.

8. Some directives are optional. If not specified DL_POLY_2 will take default values if necessary. The defaults appear in the above table.

9. The **zero** directive, enables a zero temperature simulation. This is intended as a crude energy minimizer to help relax a system before a simulation begins. It should not be thought of as a true energy minimization method.

10. The DL_POLY_2 multiple timestep option is invoked if the number appearing with the **mult** directive is greater than 2. This number (stored in the variable `multt`) specifies the number of timesteps (the multi-step) that elapse between partitions of the full Verlet neighbour list into primary and secondary atoms.

11. If a multiple time-step is used, (i.e. `multt`>2), then statistics for radial distribution functions are collected only at updates of the secondary neighbour list. The number specified on the **rdf** directive (the variable `nstbgr`) means that RDF data are accumulated at intervals of `nstbgr`×`multt` timesteps.

12. As a default, DL_POLY_2 does not store statistical data during the equilibration period. If the directive **collect** is used, equilibration data will be incorporated into the overall statistics.

13. The directive **delr** specifies the width of the border to be used in the Verlet neighbour list construction. The width is stored in the variable `delr`. The list is updated whenever two or more atoms have moved a distance of more then `delr`/2 from their positions at the last update of the Verlet list.

Users are advised to study the example CONTROL files appearing in the *data* subdirectory to see how different files are constructed.

Table 4.1: Internal Restart Key

`keyres`	meaning
0	start new simulation from CONFIG file, and assign velocities from Gaussian distribution.
1	continue current simulation
2	start new simulation from CONFIG file, and rescale velocities to desired temperature

Table 4.2: Internal Ensemble Key

`keyens`	meaning
0	Microcanonical ensemble (NVE)
1	Evans NVT ensemble
2	Berendsen NVT ensemble
3	Nosé-Hoover NVT ensemble
4	Berendsen NPT ensemble
5	Nosé-Hoover NPT ensemble
6	Berendsen N$\underline{\underline{\sigma}}$T ensemble
7	Nosé-Hoover N$\underline{\underline{\sigma}}$T ensemble
8	Potential of mean force (NVE) ensemble

Table 4.3: Internal Trajectory File Key

`keytrj`	meaning
0	coordinates only in file
1	coordinates and velocities in file
2	coordinates, velocities and forces in file

Table 4.4: Non-bonded force key

`keyfce`	meaning
odd	evaluate short-range potentials and electrostatics
even	evaluate Electrostatic potential only
Electrostatics are evaluated as follows:	
0†, 1‡	Ignore Electrostatic interactions
2, 3	Ewald summation
4, 5	distance dependent dielectric constant
6, 7	standard truncated Coulombic potential
8, 9	truncated and shifted Coulombic potential
10,11	Reaction Field electrostatics

† `keyfce` = 0 means no non-bonded terms are evaluated.

‡ `keyfce` = 1 means only short-range potentials are evaluated.

4.1.2 The CONFIG File

The CONFIG file contains the dimensions of the unit cell, the key for periodic boundary conditions and the atomic labels, coordinates, velocities and forces. This file is read by the subroutine SYSGEN. (It is also read by the subroutine SIMDEF if the **ewald precision** directive is used.) The first few records of a typical CONFIG file are shown below:

```
IceI structure 6x6x6 unit cells with proton disorder
         2         3
  26.988000000000000   0.000000000000000   0.000000000000000
 -13.494000000000000  23.372293600000000   0.000000000000000
   0.000000000000000   0.000000000000000  44.028000000000000
      OW         1
    -2.505228382         -1.484234330         -7.274585343
    0.5446573999         -1.872177437        -0.7702718106
     3515.939287          13070.74357          4432.030587
      HW         2
    -1.622622646         -1.972916834         -7.340573742
     1.507099154         -1.577400769          4.328786484
     7455.527553         -4806.880540         -1255.814536
      HW         3
    -3.258494716         -2.125627191         -7.491549620
     2.413871957         -4.336956694          2.951142896
    -7896.278327         -8318.045939         -2379.766752
      OW         4
    0.9720599243E-01     -2.503798635         -3.732081894
     1.787340483         -1.021777575         0.5473436377
     9226.455153          9445.662860          5365.202509

etc.
```

4.1.2.1 Format

The file is fixed-formatted: integers as "i10", reals as "f20.0". The header record is formatted as 80 alphanumeric characters.

4.1.2.2 Definitions of Variables

record 1		
`header`	a80	title line
record 2		
`levcfg`	integer	CONFIG file key. See table 4.5 for permitted values
`imcon`	integer	Periodic boundary key. See table 4.6 for permitted values
record 3	omitted if `imcon` = 0	
`cell(1)`	real	x component of a cell vector

`cell(2)`	real	y component of a cell vector
`cell(3)`	real	z component of a cell vector
record 4	omitted if `imcon` = 0	
`cell(4)`	real	x component of b cell vector
`cell(5)`	real	y component of b cell vector
`cell(6)`	real	z component of b cell vector
record 5	omitted if `imcon` = 0	
`cell(7)`	real	x component of c cell vector
`cell(8)`	real	y component of c cell vector
`cell(9)`	real	z component of c cell vector

Subsequent records consists of blocks of between 2 and 4 records depending on the value of the `levcfg` variable. Each block refers to one atom. The atoms must be listed sequentially in order of increasing index. Within each block the data are as follows:

record i		
`atmnam`	a8	atom name.
`index`	integer	atom index
`atmnum`	integer	atomic number
record ii		
`xxx`	real	x coordinate
`yyy`	real	y coordinate
`zzz`	real	z coordinate
record iii	included only if `levcfg` > 0	
`vxx`	real	x component of velocity
`vyy`	real	y component of velocity
`vzz`	real	x component of velocity
record iv	included only if `levcfg` > 1	
`fxx`	real	x component of force
`fyy`	real	y component of force
`fzz`	real	z component of force

Note that on **record i** only the atom name is mandatory, any other items are not read by DL_POLY_2 but may be added to aid alternative uses of the file, for example the DL_POLY_2 Graphical User Interface[20].

4.1.2.3 Further Comments

The CONFIG file has the same format as the output file REVCON (section 4.2.3). When restarting from a previous run of DL_POLY_2 (i.e. using the **restart** or **restart scale** directives in the CONTROL file - above), the CONFIG file must be replaced by the REVCON file, which is renamed as the CONFIG file. The *copy* macro in the *execute* sub-directory of DL_POLY_2 does this for you.

Table 4.5: CONFIG file key (record 2)

levcfg	meaning
0	Coordinates included in file
1	Coordinates and velocities included in file
2	Coordinates, velocities and forces included in file

Table 4.6: Periodic boundary key (record 2)

imcon	meaning
0	no periodic boundaries
1	cubic boundary conditions
2	orthorhombic boundary conditions
3	parallelepiped boundary conditions
4	truncated octahedral boundary conditions
5	rhombic dodecahedral boundary conditions
6	x-y parallelogram boundary conditions with no periodicity in the z direction
7	hexagonal prism boundary conditions

4.1.3 The FIELD File

The FIELD file contains the force field information defining the nature of the molecular forces. It is read by the subroutine SYSDEF. Excerpts from a force field file are shown below. The example is the antibiotic Valinomycin in a cluster of 146 water molecules.

```
Valinomycin Molecule with 146 SPC Waters
UNITS kcal

MOLECULES    2
Valinomycin
NUMMOLS 1
ATOMS 168
    O        16.0000     -0.4160    1
    OS       16.0000     -0.4550    1
    "          "           "        "
    "          "           "        "
    HC        1.0080      0.0580    1
    C        12.0100      0.4770    1
BONDS 78
harm   31   19 674.000     1.44900
harm   33   31 620.000     1.52600
    "    "    "    "         "
    "    "    "    "         "
harm  168   19 980.000     1.33500
harm  168  162 634.000     1.52200
CONSTRAINTS 90
   20   19    1.000017
   22   21    1.000032
    "    "     "
    "    "     "
  166  164    1.000087
  167  164    0.999968
ANGLES 312
harm   43    2   44  200.00      116.40
harm   69    5   70  200.00      116.40
  "    "    "    "     "           "
  "    "    "    "     "           "
harm   18  168  162  160.00      120.40
harm   19  168  162  140.00      116.60
DIHEDRALS 371
harm    1   43    2   44  2.3000      180.00
harm   31   43    2   44  2.3000      180.00
  "    "    "    "    "     "           "
  "    "    "    "    "     "           "
```

```
cos   149   17  161   16  10.500      180.00
cos   162   19  168   18  10.500      180.00
FINISH
SPC Water
NUMMOLS 146
ATOMS  3
    OW       16.0000     -0.8200
    HW        1.0080      0.4100
    HW        1.0080      0.4100
CONSTRAINTS  3
    1    2    1.0000
    1    3    1.0000
    2    3    1.63299
FINISH
VDW   45
C       C         lj   0.12000      3.2963
C       CT        lj   0.08485      3.2518
"       "         "     "            "
"       "         "     "            "
"       "         "     "            "
OW      OS        lj   0.15100      3.0451
OS      OS        lj   0.15000      2.9400
CLOSE
```

4.1.3.1 Format

The FIELD file is fixed-formatted. Integers are formatted as "i5", reals as "f12.0" and characters as "a4", "a8", "a40" or "a80", depending on context. The contents of the file are variable and are defined by the use of **directives**. Additional information is associated with the directives, and is free formatted as in the CONTROL file above. The file is not case sensitive.

4.1.3.2 Definitions of Variables

The file divides into three sections: general information, molecular descriptions, and non-bonded interaction descriptions, appearing in that order in the file.

4.1.3.2.1 General information

The first record in the FIELD file is the title. It must be followed by the **units** directive. Both of these are mandatory. These records may optionally be followed by the **neut** directive.

record 1

header	a80	field file header

record 2		
units	a40	Unit of energy used for input and output
record 3 (optional)		
neut	a40	activate the neutral/charge groups option for the electrostatic calculations

The energy units on the **units** directive are described by additional keywords:

a eV, for electron-volts

b kcal, for k-calories mol^{-1}

c kJ, for k-Joules mol^{-1}

d internal, for DL_POLY_2 internal units (10 J mol^{-1}).

If no units keyword is entered, DL_POLY_2 units are assumed for both input and output. The units keyword may appear anywhere on the data record provided it does not exceed column 40. The **units** directive only affects the input and output interfaces, all internal calculations are handled using DL_POLY_2 units.

4.1.3.2.2 Molecular details

It is important for the user to understand that there is an organisational correspondence between the FIELD file and the CONFIG file described above. It is required that the order of specification of molecular types and their atomic constituents in the FIELD file follows the order in which they appear in the CONFIG file. Failure to adhere to this common sequence will be detected by DL_POLY_2 and result in premature termination of the job. It is therefore essential to work from the CONFIG file when constructing the FIELD file. It is not as difficult as it sounds!

The entry of the molecular details begins with the mandatory directive:

molecules ***n***

where n is an integer specifying the number of different *types* of molecule appearing in the FIELD file. Once this directive has been encountered, DL_POLY_2 enters the *molecular description* environment in which only molecular decription keywords and data are valid.

Immediately following the **molecules** directive, are the records defining individual molecules:

1. *name-of-molecule*
   which can be any character string up to 80 characters in length. (Note: this is not a directive, just a simple character string.)

2. **nummols** ***n***
   where n is the number of times a molecule of this type appears in the simulated system. The molecular data then follow in subsequent records:

3. **atoms** ***n***
   where n indicates the number of atoms in this type of molecule. A number of records follow, each giving details of the atoms in the molecule i.e. site names, masses and charges. Each record carries the entries:

`sitnam`	a8	atomic site name
`weight`	real	atomic site mass
`chge`	real	atomic site charge
`nrept`	integer	repeat counter
`ifrz`	integer	'frozen' atom (if `ifrz`> 0)
`igrp`	integer	neutral/charge group number

   The integer `nrept` need not be specified (in which case a value of 1 is assumed.) A number greater than 1 specified here indicates that the next (`nrept` - 1) entries in the CONFIG file are ascribed the atomic characteristics given in the current record. The sum of the repeat numbers for all atoms in a molecule should equal the number specified by the **atoms** directive.

4. **shell** ***n***
   where n is the number of core-shell units. Each of the subsequent n records contains:

index 1	integer	site index of core
index 2	integer	site index of shell
spring	real	force constant of core-shell spring

   The spring force constant is entered in units of `engunit` Å^{-2}, where `engunit` is the energy unit specified in the **units** directive.

   Note that the atomic site indices referred to in this table are indices arising from numbering each atom in the molecule from 1 to the number specified in the **atoms** directive for this molecule. This same numbering scheme should be used for all descriptions of this molecule, including the **bonds**, **constraints**, **angles**, and **dihedrals** entries described below. DL_POLY_2 will itself construct the global indices for all atoms in the systems.

   This directive (and associated data records) need not be specified if the molecule contains no core-shell units.

5. **bonds** ***n***
   where n is the number of flexible chemical bonds in the molecule. Each of the subsequent n records contains:

bond key	a4	see table 4.7
index 1	integer	first atomic site in bond
index 2	integer	second atomic site in bond
variable 1	real	potential parameter see table 4.7
variable 2	real	potential parameter see table 4.7
variable 3	real	potential parameter see table 4.7
variable 4	real	potential parameter see table 4.7

The meaning of these variables is given in table 4.7. This directive (and associated data records) need not be specified if the molecule contains no flexible chemical bonds. See the note on the atomic indices appearing under the **shell** directive above.

Table 4.7: Chemical bond potentials

key	potential type	Variables (1-4)				functional form
harm **-hrm**	Harmonic	k	r_0			$U(r) = \frac{1}{2}k(r-r_0)^2$
mors **-mrs**	Morse	E_0	r_0	k		$U(r) = E_0[\{1-\exp(-k(r-r_0))\}^2 - 1]$
12-6 **-126**	12-6	A	B			$U(r) = \left(\frac{A}{r^{12}}\right) - \left(\frac{B}{r^6}\right)$
rhrm **-rhm**	Restraint	k	r_0	r_c		$U(r) = \frac{1}{2}k(r-r_0)^2 \quad \lvert r-r_0\rvert \le r_c$ $U(r) = \frac{1}{2}kr_c^2 + kr_c(\lvert r-r_0\rvert - r_c) \quad \lvert r-r_0\rvert > r_c$
quar **-qur**	Quartic	k	r_0	k'	k''	$U(r) = \frac{k}{2}(r-r_0)^2 + \frac{k'}{3}(r-r_0)^3 + \frac{k''}{4}(r-r_0)^4$

Note: bond potentials with a dash (-) as the first character of the keyword, do not contribute to the *excluded atoms list* (see section 2.1). In this case DL_POLY_2 will also calculate the nonbonded pair potentials between the described atoms, unless these are deactivated by another potential specification.

6. **constraints** ***n***
   where n is the number of constraint bonds in the molecule. Each of the following n records contains:

index 1	integer	first atomic index
index 2	integer	second atomic index
bondlength	real	constraint bond length

This directive (and associated data records) need not be specified if the molecule contains no constraint bonds. See the note on the atomic indices appearing under the **shell** directive above.

7. **pmf *b***
where b is the potential of mean force bondlength (Å). There follows the definitions of two PMF units:

   (a) **pmf unit** n_1
   where n_1 is the number of sites in the first unit. The subsequent n_1 records provide the site indices and weighting. Each record contains:

index	integer	atomic site index
weight	real	site weighting

   (b) **pmf unit** n_2
   where n_2 is the number of sites in the second unit. The subsequent n_2 records provide the site indices and weighting. Each record contains:

index	integer	atomic site index
weight	real	site weighting

   This directive (and associated data records) need not be specified if no PMF constraints are present. See the note on the atomic indices appearing under the **shell** directive above. The pmf bondlength applies to the distance between the centres of the two pmf units. The centre, $\underline{R}$, of each unit is given by

$$\underline{R} = \frac{\sum_\alpha w_\alpha \underline{r}_\alpha}{\sum_\alpha w_\alpha}$$

   where $\underline{r}_\alpha$ is a site position and w_α the site weighting. Note that the pmf constraint is intramolecular. To define a constraint between two molecules, the molecules must be described as part of the same DL_POLY "molecule". This is illustrated in test case 6, where a pmf constraint is imposed between a potassium ion and the centre of mass of a water molecule. DL_POLY_2 allows only one type of pmf constraint per system. The value of `nummols` for this molecule determines the number of pmf constraint in the system.

8. **angles *n***
where n is the number of valence angle bonds in the molecule. Each of the n records following contains:

angle key	a4	potential key. See table 4.8
index 1	integer	first atomic index

index 2	integer	second atomic index (central site)
index 3	integer	third atomic index
variable 1	real	potential parameter see table 4.8
variable 2	real	potential parameter see table 4.8

The meaning of these variables is given in table 4.8. See the note on the atomic indices appearing under the **shell** directive above. This directive (and associated data records) need not be specified if the molecule contains no angular terms.

Table 4.8: Valence Angle potentials

key	potential type	Variables (1-4)				functional form†
harm **-hrm**	Harmonic	k	θ_0			$U(\theta) = \frac{k}{2}(\theta - \theta_0)^2$
quar **-qur**	Quartic	k	θ_0	k'	k''	$U(\theta) = \frac{k}{2}(\theta - \theta_0)^2 + \frac{k'}{3}(\theta - \theta_0)^3 + \frac{k''}{4}(\theta - \theta_0)^4$
thrm **-thm**	Truncated harmonic	k	θ_0	ρ		$U(\theta) = \frac{k}{2}(\theta - \theta_0)^2 \exp[-(r_{ij}^8 + r_{ik}^8)/\rho^8]$
shrm **-shm**	Screened harmonic	k	θ_0	ρ_1	ρ_2	$U(\theta) = \frac{k}{2}(\theta - \theta_0)^2 \exp[-(r_{ij}/\rho_1 + r_{ik}/\rho_2)]$
bvs1 **-bv1**	Screened Vessal[24]	k	θ_0	ρ_1	ρ_2	$U(\theta) = \frac{k}{8(\theta-\theta_0)^2}\left\{[(\theta_0 - \pi)^2 - (\theta - \pi)^2]^2\right\}$ $\exp[-(r_{ij}/\rho_1 + r_{ik}/\rho_2)]$
bvs2 **-bv2**	Truncated Vessal[25]	k	θ_0	a	ρ	$U(\theta) = k[\theta^a(\theta - \theta_0)^2(\theta + \theta_0 - 2\pi)^2 - \frac{a}{2}\pi^{a-1}$ $(\theta - \theta_0)^2(\pi - \theta_0)^3] \exp[-(r_{ij}^8 + r_{ik}^8)/\rho^8]$
hcos **-hcs**	Harmonic Cosine	k	θ_0			$U(\theta) = \frac{k}{2}(cos(\theta) - cos(\theta_0))^2$
cos **-cos**	Cosine	A	δ	m		$U(\theta) = A[1 + cos(m\theta - \delta)]$

†θ is the a-b-c angle.

Note: valence angle potentials with a dash (-) as the first character of the keyword, do not contribute to the *excluded atoms list* (see section 2.1). In this case DL_POLY_2 will calculate the nonbonded pair potentials between the described atoms.

9. **dihedrals *n***
where n is the number of dihedral interactions present in the molecule. Each of the following n records contains:

dihedral key	a4	potential key. See table 4.9
index 1	integer	first atomic index
index 2	integer	second atomic index
index 3	integer	third atomic index
index 4	integer	fourth atomic index
variable 1	real	potential parameter see table 4.9
variable 2	real	potential parameter see table 4.9
variable 3	real	potential parameter see table 4.9
variable 4	real	1-4 electrostatic interaction scale factor.
variable 5	real	1-4 Van der Waals interaction scale factor.

The meaning of the variables 1-3 is given in table 4.9. The variables 4 and 5 specify the scaling factor for the 1-4 electrostatic and Van der Waals nonbonded interactions respectively. This directive (and associated data records) need not be specified if the molecule contains no dihedral angle terms. See the note on the atomic indices appearing under the **shell** directive above.

Table 4.9: Dihedral Angle Potentials

key	potential type	Variables (1-3)			functional form‡
cos	Cosine	A	δ	m	$U(\phi) = A[1 + \cos(m\phi - \delta)]$
harm	Harmonic	k	ϕ_0		$U(\phi) = \frac{1}{2}k(\phi - \phi_0)^2$
hcos	Harmonic cosine	k	ϕ_0		$U(\phi) = \frac{k}{2}(cos(\phi) - cos(\phi_0))^2$
cos3	Triple cosine	A_1	A_2	A_3	$U(\phi) = \frac{1}{2}A_1(1 + cos(\phi)) + \frac{1}{2}A_2(1 - cos(2\phi)) + \frac{1}{2}A_3(1 + cos(3\phi))$

‡ϕ is the a-b-c-d dihedral angle.

10. **inversions *n***
where n is the number of inversion interactions present in the molecule. Each of the following n records contains:

inversion key	a4	potential key. See table 4.10
index 1	integer	first atomic index

index 2	integer	second atomic index
index 3	integer	third atomic index
index 4	integer	fourth atomic index
variable 1	real	potential parameter see table 4.10
variable 2	real	potential parameter see table 4.10

The meaning of the variables 1-2 is given in table 4.10. This directive (and associated data records) need not be specified if the molecule contains no inversion angle terms. See the note on the atomic indices appearing under the **shell** directive above.

Table 4.10: Inversion Angle Potentials

key	potential type	Variables (1-2)		functional form‡
harm	Harmonic	k	ϕ_0	$U(\phi) = \frac{1}{2}k(\phi - \phi_0)^2$
hcos	Harmonic cosine	k	ϕ_0	$U(\phi) = \frac{k}{2}(cos(\phi) - cos(\phi_0))^2$
plan	Planar	A		$U(\phi) = A[1 - \cos(\phi)]$

‡ϕ is the inversion angle.

11. **rigid *n***
where n is the number of rigid units in the molecule. It is followed by at least n records, each specifying the sites in a rigid unit:

m	integer	number of sites in rigid unit
site 1	integer	first site atomic index
site 2	integer	second site atomic index
site 3	integer	third site atomic index
..	..	*etc.*
site m	integer	m'th site atomic index

Up to 15 sites can be specified on the first record. Additional records are used if necessary. Up to 16 sites are specified per record thereafter.

This directive (and associated data records) need not be specified if the molecule contains no rigid units. See the note on the atomic indices appearing under the **shell** directive above.

12. **teth *n***
where n is the number of tethered atoms in the molecule. It is followed by n records specifying the tethered sites in the molecule:

tether key	a4	tethering potential key see table 4.11
index	integer	atomic index
variable 1	real	potential parameter see table 4.11
variable 2	real	potential parameter see table 4.11
variable 3	real	potential parameter see table 4.11
variable 4	real	potential parameter see table 4.11

This directive (and associated data records) need not be specified if the molecule contains no tethered atoms. See the note on the atomic indices appearing under the **shell** directive above.

Table 4.11: Tethering potentials

key	potential type	Variables (1-3)			functional form
harm	Harmonic	k			$U(r) = \frac{1}{2}kr^2$
rhrm	Restraint	k	r_c		$U(r) = \frac{1}{2}kr^2 \quad r \le r_c$ $U = \frac{1}{2}kr_c^2 + kr_c(r - r_c) \quad r > r_c$
quar	Quartic	k	k'	k''	$U(r) = \frac{k}{2}r^2 + \frac{k'}{3}r^3 + \frac{k''}{4}r^4$

13. **finish**
    This directive is entered to signal to DL_POLY_2 that the entry of the details of a molecule has been completed.

    The entries for a second molecule may now be entered, beginning with the *name-of-molecule* record and ending with the **finish** directive.

    The cycle is repeated until all the types of molecules indicated by the **molecules** directive have been entered.

The user is recommended to look at the example FIELD files in the *data* directory to see how typical FIELD files are constructed.

4.1.3.3 Non-bonded Interactions

Non-bonded interactions are identified by atom types as opposed to specific atomic indices. The first type of non-bonded potentials are the pair potentials. The input of pair potential data is signalled by the directive:

vdw ***n***

where n is the number of pair potentials to be entered. There follows n records, each specifying a particular pair potential in the following manner:

atmnam 1	a8	first atom type
atmnam 2	a8	second atom type
key	a4,1X	potential key. See table 4.12
variable 1	real	potential parameter see table 4.12
variable 2	real	potential parameter see table 4.12
variable 3	real	potential parameter see table 4.12
variable 4	real	potential parameter see table 4.12
variable 5	real	potential parameter see table 4.12

The variables pertaining to each potential are described in table 4.12.**Note** that there is an empty column after the potential key. This means that the potential paramaters are enterd in columns 22 to 81. Note that any pair potential not specified in the FIELD file, will be assumed to be zero. Note also that the Sutton-Chen potential for metals is classified as a pair potential for input purposes.

The specification of three body potentials is initiated by the directive:

tbp *n*

where n is the number of three-body potentials to be entered. There follows n records, each specifying a particular three body potential in the following manner:

atmnam 1	a8	first atom type
atmnam 2	a8	second atom type (central site)
atmnam 3	a8	third atom type
key	a4	potential key. See table 4.13
variable 1	real	potential parameter see table 4.13
variable 2	real	potential parameter see table 4.13
variable 3	real	potential parameter see table 4.13
variable 4	real	potential parameter see table 4.13
variable 5	real	cutoff range for this potential (Å)

The variables pertaining to each potential are described in table 4.13. Note that the fifth variable is the range at which the three body potential is truncated. The distance is in Å, measured from the central atom.

The specification of four body potentials is initiated by the directive:

fbp *n*

where n is the number of four-body potentials to be entered. There follows n records, each specifying a particular four-body potential in the following manner:

atmnam 1	a8	first atom type (central site)
atmnam 2	a8	second atom type
atmnam 3	a8	third atom type
atmnam 4	a8	fourth atom type
key	a4	potential key. See table 4.14
variable 1	real	potential parameter see table 4.14
variable 2	real	potential parameter see table 4.14
variable 3	real	cutoff range for this potential (Å)

The variables pertaining to each potential are described in table 4.14. Note that the third variable is the range at which the four-body potential is truncated. The distance is in Å, measured from the central atom.

4.1.3.4 External Field

The presence of an external field is flagged by the **extern** directive. The next line in the FIELD file should have another directive indicating what type of field is to be applied. On the following lines comes the `mxfld` parameters, five per line, that describe the field. In the include files supplied with DL_POLY_2 `mxfld` is set to 10.
The variables pertaining to each potential are described in table 4.15.

4.1.3.5 Closing the FIELD File

The FIELD file must be closed with the directive:

close

which signals the end of the force field data. Without this directive DL_POLY_2 will abort.

4.1.4 The REVOLD File

This file contains statistics arrays from a previous job. It is not required if the current job is not a continuation of a previous run (ie. if the **restart** directive is not present in the CONTROL file - see above). The file is unformatted and therefore not readable by normal people. DL_POLY_2 normally produces the file REVIVE (see section 4.2.4) at the end of a job which contains the statistics data. REVIVE should be copied to REVOLD before a continuation run commences. This may be done by the *copy* macro supplied in the *execute* sub-directory of DL_POLY_2 .

4.1.4.1 Format

The REVOLD file is unformatted. All variables appearing are written in native real*8 representation. Nominally integer quantities (e.g. the timestep number `nstep`) are represented by the the nearest real number. The contents are as follows (the dimensions of array variables are given in brackets, in terms of parameters from the DL_PARAMS.INC file - see section 7.1.1).

record 1:
- `nstep` timestep of final configuration
- `numacc` number of configurations used in averages
- `numrdf` number of configurations used in rdf averages
- `chit` relaxation time of thermostat
- `chip` relaxation time of barostat
- `conint` conserved quantity for selected ensemble
- `nzden` number of configurations used in z density

record 2:
- `eta` scaling factors for simulation cell matrix elements (9)

record 3:
- `stpval` instantaneous values of thermodynamic variables (`mxnstk`)

record 4:
- `sumval` average values of thermodynamic variables (`mxnstk`)

record 5:
- `ssqval` fluctuation (squared) of thermodynamic variables (`mxnstk`)

record 6:
- `zumval` running totals of thermodynamic variables (`mxnstk`)

record 7:
- `ravval` rolling averages of thermodynamic variables (`mxnstk`)

record 8:
- `stkval` stacked values of thermodynamic variables (`mxstak`×`mxnstk`)

record 9:
- `xx0` atomic x-coordinates at MSD time origin (`mxatms`)
- `yy0` atomic y-coordinates at MSD time origin (`mxatms`)
- `zz0` atomic z-coordinates at MSD time origin (`mxatms`)

record 10:
- `xxs` instantaneous atomic x-coordinates for MSD (`mxatms`)
- `yys` instantaneous atomic y-coordinates for MSD (`mxatms`)
- `zzs` instantaneous atomic z-coordinates for MSD (`mxatms`)

record 11:
- `rdf` (Optional) RDF array (`mxrdf`×`mxvdw`)

record 12:
- `zdens` (Optional) z-density array (`mxrdf`×`mxsvdw`)

4.1.4.2 Further Comments

Note that recompiling DL_POLY_2 with a different DL_PARAMS.INC file, may render any existing REVOLD file unreadable by the code.

4.1.5 The TABLE File

The TABLE file provides an alternative way of reading in the short range potentials - in tabular form. This is particularly useful if an analytical form of the potential does not exist or is too complicated to specify in the FORGEN subroutine. The table file is read by the subroutine FORTAB (see chapter 7).

The option of using tabulated potentials is specified in the FIELD file (see above). The specific potentials that are to be tabulated are indicated by the use of the **tab** keyword on the record defining the short range potential (see table 4.12). The directive **vdwtable** may be used in place of **vdw** to indicate that one or more of the short ranged potentials is specified in the form of a table.

4.1.5.1 Format

The file is fixed-formatted with integers as "i10", reals as "e15.8". Character variables are read as "a8". The header record is formatted as 80 alphanumeric characters.

4.1.5.2 Definitions of Variables

record 1		
`header`	a80	file header
record 2		
`delpot`	real	mesh resolution in Å
`cutpot`	real	cutoff used to define tables Å
`ngrid`	integer	number of grid points in tables

The subsequent records define each tabulated potential in turn, in the order indicated by the specification in the FIELD file. Each potential is defined by a header record and a set of data records with the potential and force tables.

header record:		
`atom 1`	a8	first atom type
`atom 2`	a8	second atom type
potential data records:	($number\ of\ data\ records = Int((\texttt{ngrid}+3)/4)$)	
`data 1`	real	data item 1
`data 2`	real	data item 2
`data 3`	real	data item 3
`data 4`	real	data item 4
force data records:	($number\ of\ data\ records = Int((\texttt{ngrid}+3)/4)$)	
`data 1`	real	data item 1

`data 2`	real	data item 2
`data 3`	real	data item 3
`data 4`	real	data item 4

4.1.5.3 Further Comments

It should be noted that the number of grid points in the TABLE file should not be less than the number of grid points DL_POLY_2 is expecting. (This number is given by the parameter `mxgrid` in the DL_PARAMS.INC file - see section 7.1.1.) DL_POLY_2 will re-interpolate the tables if `ngrid`≥`mxgrid`, but will abort if `ngrid`<`mxgrid`.

The potential and force tables are used to fill the internal arrays `vvv` and `ggg` respectively (see section 2.3.1). The contents of force arrays are derived from the potential via the formula:

$$G(r) = -r\frac{\partial}{\partial r}U(r).$$

Note this is *not* the same as the true force.

4.2 The OUTPUT Files

DL_POLY_2 produces up to seven output files: HISTORY, OUTPUT, REVCON, REVIVE, RDFDAT, ZDNDAT and STATIS. These respectively contain: a dump file of atomic coordinates, velocities and forces; a summary of the simulation; the restart configuration; statistics accumulators; radial distribution data, Z-density data and a statistical history.

4.2.1 The HISTORY File

The HISTORY file is the dump file of atomic coordinates, velocities and forces. Its principal use is for off-line analysis. The file is written by the subroutines TRAJECT or TRAJECT_U. The control variables for this file are `ltraj, nstraj, istraj` and `keytrj` which are created internally, based on information read from the **traj** directive in the CONTROL file (see above). The HISTORY file will be created only if the directive **traj** appears in the CONTROL file. Note that the HISTORY file can be written in either a formatted or unformatted version. We describe each of these separately below.

The HISTORY file can become *very* large, especially if it is formatted. For serious simulation work it is recommended that the file be written to a scratch disk capable of accommodating a large data file. Alternatively the file may be written as unformatted (below), which has the additional advantage of speed. However, writing an unformatted file has the disadvantage that the file may not be readily readable except by the machine on which it was created. This is particularly important if graphical processing of the data is required.

4.2.1.1 The Formatted HISTORY File

The formatted HISTORY file is written by the subroutine TRAJECT and has the following structure.

record 1 (a80)

`header`	a80	file header

record 2 (2i10)

`keytrj`	integer	trajectory key (see table 4.3)
`imcon`	integer	periodic boundary key (see table 4.6)
`natms`	integer	number of atoms in simulation cell

For timesteps greater than `nstraj` the HISTORY file is appended at intervals specified by the **traj** directive in the CONTROL file, with the following information for each configuration:

record i (a8,4i10,f12.6)

`timestep`	a8	the character string "timestep"
`nstep`	integer	the current time-step
`natms`	integer	number of atoms in configuration
`keytrj`	integer	trajectory key (again)

`imcon`	integer	periodic boundary key (again)
`tstep`	real	integration timestep
record ii (3g12.4) for `imcon` > 0		
`cell(1)`	real	x component of a cell vector
`cell(2)`	real	y component of a cell vector
`cell(3)`	real	z component of a cell vector
record iii (3g12.4) for `imcon` > 0		
`cell(4)`	real	x component of b cell vector
`cell(5)`	real	y component of b cell vector
`cell(6)`	real	z component of b cell vector
record iv (3g12.4) for `imcon` > 0		
`cell(7)`	real	x component of c cell vector
`cell(8)`	real	y component of c cell vector
`cell(9)`	real	z component of c cell vector

This is followed by the configuration for the currect timestep. i.e. for each atom in the system the following data are included:

record a (a8,i10,2f12.6)		
`atmnam`	a8	atomic label
`iatm`	i10	atom index
`weight`	f12.6	atomic mass (a.m.u.)
`charge`	f12.6	atomic charge (e)
record b (3e12.4)		
`xxx`	real	x coordinate
`yyy`	real	y coordinate
`zzz`	real	z coordinate
record c (3e12.4) only for `keytrj` > 0		
`vxx`	real	x component of velocity
`vyy`	real	y component of velocity
`vzz`	real	z component of velocity
record d (3e12.4) only for `keytrj` > 1		
`fxx`	real	x component of force
`fyy`	real	y component of force
`fzz`	real	z component of force

Thus the data for each atom is a minimum of two records and a maximum of 4.

4.2.1.2 The Unformatted HISTORY File

The unformatted HISTORY file is written by the subroutine TRAJECT_U and has the following structure:

record 1
`header` configuration name (character*80)
record 2
`natms` number of atoms in the configuration (real*8)
record 3
`atname(1,...,natms)` atom names or symbols (character*8)
record 4
`weight(1,...,natms)` atomic masses (real*8)
record 5
`charge(1,...,natms)` atomic charges (real*8)

For time-steps greater than `nstraj`, the HISTORY file is appended, at intervals specified by the **traj** directive in the CONTROL file, with the following information:

record i
`nstep` the current time-step (real*8)
`natms` number of atoms in configuration (real*8)
`keytrj` trajectory key (real*8)
`imcon` image convention key (real*8)
`tstep` integration timestep (real*8)
record ii for `imcon` > 0
`cell(1,...,9)` a, b and c cell vectors (real*8)
record iii
`xxx(1,...,natms)` atomic x-coordinates (real*8)
record iv
`yyy(1,...,natms)` atomic y-coordinates (real*8)
record v
`zzz(1,...,natms)` atomic z-coordinates (real*8)
record vi only for `keytrj`> 0
`vxx(1,...,natms)` atomic velocities x-component (real*8)
record vii only for `keytrj`> 0
`vyy(1,...,natms)` atomic velocities y-component (real*8)
record viii only for `keytrj`> 0
`vzz(1,...,natms)` atomic velocities z-component (real*8)
record ix only for `keytrj`> 1
`fxx(1,...,natms)` atomic forces x-component (real*8)
record x only for `keytrj`> 1
`fyy(1,...,natms)` atomic forces y-component (real*8)
record xi only for `keytrj`> 1
`fzz(1,...,natms)` atomic forces z-component (real*8)

Note the implied conversion of integer variables to real on record i.

4.2.2 The OUTPUT File

The job output consists of 7 sections: Header; Simulation control specifications; Force field specification; Summary of the initial configuration; Simulation progress; Summary of statistical data; Sample of the final configuration; and Radial distribution functions. These sections are written by different subroutines at various stages of a job. Creation of the OUTPUT file *always* results from running DL_POLY_2 . It is meant to be a human readable file, destined for hardcopy output.

4.2.2.1 Header

Gives the DL_POLY_2 version number, the number of processors used and a title for the job as given in the header line of the input file CONTROL. This part of the file is written from the subroutines DLPOLY and SIMDEF

4.2.2.2 Simulation Control Specifications

Echoes the input from the CONTROL file. Some variables may be reset if illegal values were specified in the CONTROL file. This part of the file is written from the subroutine SIMDEF.

4.2.2.3 Force Field Specification

Echoes the FIELD file. A warning line will be printed if the system is not electrically neutral. This warning will appear immediately before the non-bonded short-range potential specifications. This part of the file is written from the subroutine SYSDEF.

4.2.2.4 Summary of the Initial Configuration

This part of the file is written from the subroutine SYSGEN. It states the periodic boundary specification, the cell vectors and volume (if appropriate) and the initial configuration of (a maximum of) 20 atoms in the system. The configuration information given is based on the value of `levcfg` in the CONFIG file. If `levcfg` is 0 (or 1) positions (and velocities) of the 20 atoms are listed. If `levcfg` is 2 forces are also written out.

For periodic systems this is followed by the long range corrections to the energy and pressure.

4.2.2.5 Simulation Progress

This part of the file is written by the DL_POLY_2 root segment DLPOLY. The header line is printed at the top of each page as:

```
------------------------------------------------------------------------------------------------

    step   eng_tot  temp_tot   eng_cfg   eng_vdw   eng_cou   eng_bnd   eng_ang   eng_dih   eng_tet
time(ps)    eng_pv  temp_rot   vir_cfg   vir_vdw   vir_cou   vir_bnd   vir_ang   vir_con   vir_tet
cpu  (s)    volume  temp_shl   eng_shl   vir_shl     alpha      beta   gamma   vir_pmf     press
```

The labels refer to :

line 1

step	MD step number
`eng_tot`	total internal energy of the system
`temp_tot`	system temperature
`eng_cfg`	configurational energy of the system
`eng_vdw`	configurational energy due to short-range potentials
`eng_cou`	configurational energy due to electrostatic potential
`eng_bnd`	configurational energy due to chemical bond potentials
`eng_ang`	configurational energy due to valence angle and three-body potentials
`eng_dih`	configurational energy due to dihedral inversion and four-body potentials
`eng_tet`	configurational energy due to tethering potentials

line 2

`time(ps)`	elapsed simulation time (ps) since the beginning of the job
`eng_pv`	enthalpy of system
`temp_rot`	rotational temperature
`vir_cfg`	total configurational contribution to the virial
`vir_vdw`	short range potential contribution to the virial
`vir_cou`	electrostatic potential contribution to the virial
`vir_bnd`	chemical bond contribution to the virial
`vir_ang`	angular and three body potentials contribution to the virial
`vir_con`	constraint bond contribution to the virial
`vir_tet`	tethering potential contribution to the virial

line 3

`cpu (s)`	elapsed cpu time since the beginning of the job
`volume`	system volume
`temp_shl`	core-shell temperature
`eng_shl`	configurational energy due to core-shell potentials
`vir_shl`	core-shell potential contribution to the virial
`alpha`	angle between b and c cell vectors
`beta`	angle between c and a cell vectors
`gamma`	angle between a and b cell vectors
`vir_pmf`	Potential of mean force constraint contribution to the virial
`press`	pressure

Note: The total internal energy of the system (variable `tot_energy`) includes all contributions to the energy (including system extensions due to thermostats etc.) It is nominally the *conserved variable* of the system, and is not to be confused with conventional system energy, which is a sum of the kinetic and configuration energies.

The interval for printing out these data is determined by the directive **print** in the CONTROL file. At each time-step that printout is requested the instantaneous values of

the above statistical variables are given in the appropriate columns. Immediately below these three lines of output the rolling averages of the same variables are also given. The maximum number of time-steps used to calculate the rolling averages is determined by the parameter `mxstak` in the DL_PARAMS.INC file (see section 7.1.1). The working number of time-steps for rolling averages is controlled by the directive **stack** in file CONTROL (see above). The default value is `mxstak`.

Energy Units: The energy unit for the data appearing in the OUTPUT is defined by the **units** directive appearing in the CONTROL file.

Pressure units: The unit of pressure is *k bar*, irrespective of what energy unit is chosen.

4.2.2.6 Summary of Statistical Data

This portion of the OUTPUT file is written from the subroutine RESULT. The number of time-steps used in the collection of statistics is given. Then the averages over the production portion of the run are given for the variables described in the previous section. The root mean square variation in these variables follow on the next two lines. The energy and pressure units are as for the preceeding section.

Also provided in this section is an estimate of the diffusion coefficient for the different species in the simulation, which is determined from a *single time origin* and is therefore very approximate. Accurate determinations of the diffusion coefficients can be obtained using the MSD utility program, which processes the HISTORY file (see chapter 6).

If an NPT or N$\underline{\underline{\sigma}}$T simulation is performed the OUTPUT file also provides the mean stress (pressure) tensor and mean simulation cell vectors.

4.2.2.7 Sample of Final Configuration

The positions, velocities and forces of the 20 atoms used for the sample of the initial configuration (see above) are given. This is written by the subroutine RESULT.

4.2.2.8 Radial Distribution Functions

If both calculation and printing of radial distribution functions have been requested (by selecting directives **rdf** and **print rdf** in the CONTROL file) radial distribution functions are printed out. This is written from the subroutine RDF1. First the number of time-steps used for the collection of the histograms is stated. Then each function is given in turn. For each function a header line states the atom types ('a' and 'b') represented by the function. Then r, $g(r)$ and $n(r)$ are given in tabular form. Output is given from 2 entries before the first non-zero entry in the $g(r)$ histogram. $n(r)$ is the average number of atoms of type 'b' within a sphere of radius r around an atom of type 'a'. Note that a readable version of these data is provided by the RDFDAT file (below).

4.2.2.9 Z Density Profile

If both calculation and printing of Z density profiles has been requested (by selecting directives **zden** and **print rdf** in the CONTROL file Z density profiles are printed out as the last part of the OUTPUT file. This is written by the subroutine ZDEN1. First the number of time-steps used for the collection of the histograms is stated. Then each function is given in turn. For each function a header line states the atom type represented by the function. Then z, $\rho(z)$ and $n(z)$ are given in tabular form. Output is given from $Z = [-L/2, L/2]$ where L is the length of the MD cell in the Z direction and $\rho(z)$ is the mean number density. $n(z)$ is the running integral from $-L/2$ to z of (xy cell area)$\rho(s)ds$. Note that a readable version of these data is provided by the ZDNDAT file (below).

4.2.3 The REVCON File

This file is formatted and written by the subroutine REVIVE. REVCON is the restart configuration file. The file is written every `ndump` time steps in case of a system crash during execution and at the termination of the job. A successful run of DL_POLY_2 will always produce a REVCON file, but a failed job may not produce the file if an insufficient number of timesteps have elapsed. `ndump` is a parameter defined in the DL_PARAMS.INC file found in the *source* directory of DL_POLY_2 (section 7.1.1). Changing `ndump` necessitates recompiling DL_POLY_2 . REVCON is identical in format to the CONFIG input file (see section 4.1.2). REVCON should be renamed CONFIG to continue a simulation from one job to the next. This is done for you by the *copy* macro supplied in the *execute* directory of DL_POLY_2 .

4.2.4 The REVIVE File

This file is unformatted and written by the subroutine REVIVE. It contains the accumulated statistical data. It is updated whenever the file REVCON is updated (see previous section). REVIVE should be renamed REVOLD to continue a simulation from one job to the next. This is done by the *copy* macro supplied in the *execute* directory of DL_POLY_2 . In addition, to continue a simulation from a previous job the **restart** keyword must be included in the CONTROL file.

The format of the REVIVE file is identical to the REVOLD file described in section 4.1.4.

4.2.5 The RDFDAT File

This is a formatted file containing em Radial Distribution Function (RDF) data. Its contents are as follows:

record 1		
`cfgname`	character (A80)	configuration name
record 2		
`ntpvdw`	integer (i10)	number of RDFs in file

`mxrdf`	integer (i10)	number of data points in each RDF

There follow the data for each individual RDF i.e. *ntpvdw* times. The data supplied are as follows:

first record

`atname 1`	character (A8)	first atom name
`atname 2`	character (A8)	second atom name

following records (*mxrdf* records)

`radius`	real (e14)	interatomic distance (A)
`g(r)`	real (e14)	RDF at given radius.

Note the RDFDAT file is optional and appears when the **print rdf** option is specified in the CONTROL file.

4.2.6 The ZDNDAT File

This is a formatted file containing the Z-density data. Its contents are as follows:

record 1

`cfgname`	character (A80)	configuration name

record 2

`mxrdf`	integer (i10)	number of data points in the Z-density function

following records (*mxrdf* records)

`z`	real (e14)	distance in z direction (A)
$\rho(z)$	real (e14)	Z-density at given height `z`

Note the ZDNDAT file is optional and appears when the **print rdf** option is specified in the CONTROL file.

4.2.7 The STATIS File

The file is formatted, with integers as "i10" and reals as "e14.6". It is written by the subroutine STATIC. It consists of two header records followed by many data records of statistical data.

record 1

`cfgname`	character	configuration name

record 2

`string`	character	energy units

Data records

Subsequent lines contain the instantaneous values of statistical variables dumped from the array `stpval`. A specified number of entries of `stpval` are written in the format "(1p,5e14.6)". The number of array elements required (determined by the parameter `mxnstk` in the DL_PARAMS.INC file) is

$$\begin{aligned} \texttt{mxnstk} \geq \quad & 27 + \texttt{ntpatm}(\text{number of unique atomic sites}) \\ & +9(\text{if stress tensor calculated}) \\ & +9(\text{if constant pressure simulation requested}) \end{aligned}$$

The STATIS file is appended at intervals determined by the **stats** directive in the CONTROL file. The energy unit is as specified in the CONTROL file with the the **units** directive, and are compatible with the data appearing in the OUTPUT file. The contents of the appended information is:

record i		
`nstep`	integer	current MD time-step
`time`	real	elapsed simulation time = `nstep`$\times\Delta t$
`nument`	integer	number of array elements to follow
record ii `stpval`(1) – `stpval`(5)		
`engcns`	real	total extended system energy (i.e. the conserved quantity)
`temp`	real	system temperature
`engcfg`	real	configurational energy
`engsrp`	real	short range potential energy
`engcpe`	real	electrostatic energy
record iii `stpval`(6) – `stpval`(10)		
`engbnd`	real	chemical bond energy
`engang`	real	valence angle and 3-body potential energy
`engdih`	real	dihedral interaction energy
`engtet`	real	tethering energy
`enthal`	real	enthalpy (total energy + PV)
record iv `stpval`(11) – `stpval`(15)		
`tmprot`	real	rotational temperature
`vir`	real	total virial
`virsrp`	real	short-range virial
`vircpe`	real	electrostatic virial
`virbnd`	real	bond virial
record v `stpval`(16) -`stpval`(20)		
`virang`	real	valence angle and 3-body virial
`vircon`	real	constraint virial
`virtet`	real	tethering virial
`volume`	real	volume
`tmpshl`	real	core-shell temperature

record vi `stpval`(21) -`stpval`(25)		
`engshl`	real	core-shell potential energy
`virshl`	real	core-shell virial
`alpha`	real	MD cell angle α
`beta`	real	MD cell angle β
`gamma`	real	MD cell angle γ
record vii `stpval`(26) -`stpval`(27)		
`virpmf`	real	Potential of Mean Force virial
`press`	real	pressure
the next `ntpatm` **entries**		
`amsd(1)`	real	mean squared displacement of first atom types
`amsd(2)`	real	mean squared displacement of second atom types
`...`	...	...
`amsd(ntpatm)`	real	mean squared displacement of last atom types
the next 9 entries - *if* the stress tensor is calculated		
`stress(1)`	real	xx component of stress tensor
`stress(2)`	real	xy component of stress tensor
`stress(3)`	real	xz component of stress tensor
`stress(4)`	real	yx component of stress tensor
`...`	real	...
`stress(9)`	real	zz component of stress tensor
the next 9 entries - *if* a NPT simulation is undertaken		
`cell(1)`	real	x component of a cell vector
`cell(2)`	real	y component of a cell vector
`cell(3)`	real	z component of a cell vector
`cell(4)`	real	x component of b cell vector
`...`	real	...
`cell(9)`	real	z component of c cell vector

Note. The stress tensor is calculated only if the code is compiled with the "-STRESS" option (see section 3.2.1). Cell shape varying constant pressure simulations (keyword **ensemble nst ...** in the CONTROL file) are only possible if the stress tensor is calculated. If isotropic constant pressure simulations are required, where the cell volume but not the shape may vary, (keyword **ensemble npt ...**) the stress tensor need not be calculated.

Table 4.12: Definition of pair potential functions and variables

key	potential type	Variables (1-5)					functional form
12-6	12-6	A	B				$U(r) = \left(\frac{A}{r^{12}}\right) - \left(\frac{B}{r^6}\right)$
lj	Lennard-Jones	ϵ	σ				$U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$
nm	n-m	E_o	n	m	r_0		$U(r) = \frac{E_o}{(n-m)}\left[m\left(\frac{r_o}{r}\right)^n - n\left(\frac{r_o}{r}\right)^m\right]$
buck	Buckingham	A	ρ	C			$U(r) = A\ \exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6}$
bhm	Born-Huggins -Meyer	A	B	σ	C	D	$U(r) = A\ \exp[B(\sigma - r)] - \frac{C}{r^6} - \frac{D}{r^8}$
hbnd	12-10 H-bond	A	B				$U(r) = \left(\frac{A}{r^{12}}\right) - \left(\frac{B}{r^{10}}\right)$
snm	Shifted force† $U(r) = \frac{\alpha E_o}{(n-m)}\times$ n-m [27]	E_o	n	m	r_0	r_c ‡	$\left[m\beta^n\left\{\left(\frac{r_o}{r}\right)^n - \left(\frac{1}{\gamma}\right)^n\right\} - n\beta^m\left\{\left(\frac{r_o}{r}\right)^m - \left(\frac{1}{\gamma}\right)^m\right\}\right]$ $+\frac{nm\alpha E_o}{(n-m)}\left(\frac{r-\gamma r_o}{\gamma r_o}\right)\left\{\left(\frac{\beta}{\gamma}\right)^n - \left(\frac{\beta}{\gamma}\right)^m\right\}$
stch	Sutton-Chen	ϵ	a	n	m	C	$U_i(r) = \epsilon\left[\left(\frac{a}{r}\right)^n - \frac{C}{2}\sqrt{\rho_i}\right]$ $\rho_i = \sum_j\left(\frac{a}{r_{ij}}\right)^m$
tab	Tabulation						tabulated potential

† Note: in this formula the terms α, β and γ are compound expressions involving the variables E_o, n, m, r_0 and r_c. See section 2.3.1 for further details.

‡ Note: r_c defaults to the general van der Waals cutoff (`rvdw` or `rcut`) if it is set to zero or not specified or not specified in the FIELD file.

Table 4.13: Three-body potentials

key	potential type	Variables (1-4)				functional form†
thrm	Truncated harmonic	k	θ_0	ρ		$U(\theta) = \frac{k}{2}(\theta - \theta_0)^2 \exp[-(r_{ij}^8 + r_{ik}^8)/\rho^8]$
shrm	Screened harmonic	k	θ_0	ρ_1	ρ_2	$U(\theta) = \frac{k}{2}(\theta - \theta_0)^2 \exp[-(r_{ij}/\rho_1 + r_{ik}/\rho_2)]$
bvs1	Screened Vessal[24]	k	θ_0	ρ_1	ρ_2	$U(\theta) = \frac{k}{8(\theta-\theta_0)^2}\left\{[(\theta_0 - \pi)^2 - (\theta - \pi)^2]^2\right\}$ $\exp[-(r_{ij}/\rho_1 + r_{ik}/\rho_2)]$
bvs2	Truncated Vessal[25]	k	θ_0	a	ρ	$U(\theta) = k[\theta^a(\theta - \theta_0)^2(\theta + \theta_0 - 2\pi)^2 - \frac{a}{2}\pi^{a-1}$ $(\theta - \theta_0)^2(\pi - \theta_0)^3] \exp[-(r_{ij}^8 + r_{ik}^8)/\rho^8]$
hbnd	H-bond [7]	D_{hb}	R_{hb}			$U(\theta) = D_{hb} cos^4(\theta)[5(R_{hb}/r_{jk})^{12} - 6(R_{hb}/r_{jk})^{10}]$

†θ is the a-b-c angle.

Table 4.14: Four-body Potentials

key	potential type	Variables (1-2)		functional form‡
harm	Harmonic	k	ϕ_0	$U(\phi) = \frac{1}{2}k(\phi - \phi_0)^2$
hcos	Harmonic cosine	k	ϕ_0	$U(\phi) = \frac{k}{2}(cos(\phi) - cos(\phi_0))^2$
plan	Planar	A		$U(\phi) = A[1 - \cos(\phi)]$

‡ϕ is the inversion angle.

Table 4.15: External fields

key	potential type	Variables (1-4)				functional form†
elec	Electric field	E_x	E_y	E_z		$\underline{F} = q.\underline{E}$
oshm	Oscillating Shear	A	n			$\underline{F}_x = Acos(2n\pi.z/L_z)$
shrx	Continuous Shear	A	z_0			$\mid z \mid > z_0$: $\underline{v}_x = (1/2)A(\mid z \mid /z)$
grav	Gravitational Field	G_x	G_y	G_z		$\underline{F} = m.\underline{G}$
magn	Magnetic Field	H_x	H_y	H_z		$\underline{F} = q(\underline{v} \times \underline{H})$
sphr	Containing Sphere	A	R_0	n	R_{cut}	$r > R_{\text{cut}}$: $\underline{F} = A(R_0 - r)^{-n}$

Chapter 5

DL_POLY_2 Examples

Scope of Chapter

This chapter describes the standard test cases for DL_POLY_2 , the input and output files for which are in the *data* sub-directory.

5.1 DL_POLY Examples

5.1.1 Test Cases

The following example data sets (both input and output) are stored in the subdirectory *data*. These are provided so that you may check that your version of DL_POLY is working correctly. All the jobs are short and should require no more than a few minutes execution time, even on a single processor computer. The output files are stored in compressed format. The test cases can be run by typing

select n

from the *execute* directory, where n is the number of the test case. The *select* macro will copy the appropriate CONTROL, CONFIG, and FIELD files to the *execute* directory ready for execution. The output files OUTPUT, REVCON and STATIS may be compared with the files supplied in the *data* directory.

The example output files provided in the *data* directory were obtained on 4 processors of an IBM SP/2 parallel system (120 MHz P2SC 'thin' nodes). The program was compiled with the three point interpolation option.

It should be noted that the potentials and the simulation conditions used in the following test cases are chosen to demonstrate functionality only. **They are not necessarily appropriate for serious simulation of the test systems.** Note also that the DL_POLY_2 Graphical User Interface [20] provides a convenient means for running and viewing these test cases.

5.1.1.1 Test Case 1: $KNaSi_2O_5$

Potassium Sodium disilicate glass ($NaKSi_2O_5$) using two and three body potentials. Some of the two body potentials are read from the TABLE file. Electrostatics are handled by a multiple timestep Ewald sum method. Cubic periodic boundaries are in use.

5.1.1.2 Test Case 2: Metal simulation with Sutton Chen potentials

FCC Aluminium using Sutton-Chen potentials. Temperature is controlled by the method of Gaussian constraints.

5.1.1.3 Test Case 3: An antibiotic in water

Valinomycin in 1223 spc water molecules. The temperature is controlled by a Nosé-Hoover thermostat while electrostatics are handled by a shifted Coulombic potential. The water is defined as a rigid body while bond constraints are applied to all chemical bonds in the valinomycin. Truncated octahedral boundary conditions are used.

5.1.1.4 Test Case 4: Shell model of water

256 molecules of water with a polarizable oxygen atom. Temperature is controlled by the Berendsen thermostat while electrostatics are handled by the reaction field method with

a "charge group" cutoff scheme. "Slab" period boundary conditions are used. The water molecule (apart from the shell) is treated as a rigid body.

5.1.1.5 Test Case 5: Shell model of $MgCl_2$ at constant pressure

Dynamical Shell model simulation of $MgCl_2$. Temperature and pressure are controlled by a Berendsen thermostat and barostat. An Ewald sum is used with cubic periodic boundary conditions.

5.1.1.6 Test Case 6: PMF calculation

Potential of mean force calculation of a potassium ion in SPC water. Electrostatics are handled by the Ewald sum. The water is treated as a constrained triangle.

5.1.1.7 Test Case 7: Linked rigid bodies at constant pressure

8 biphenyl molecules in cubic boundary conditions. Temperature and pressure are controlled by a Hoover type thermostat and barostat. Each phenyl ring is treated as a rigid body, with a constraint bond to the other ring of the molecule. In the centre of each ring are three massless charge sites which imparts a quadrupole moment to the ring.

5.1.1.8 Test Case 8: An osmosis experiment with a semi permeable membrane

The membrane is a collection of tethered sites interconnected by harmonic springs. There are no electrostatic forces in the system. The simulation is run with the Hoover anisotropic constant presure algorithm.

5.1.1.9 Test Case 9: A surfactant at the air-water interface

The system is comprised of 32 surfactant molecules (trimethylaminododecane bromide or TAB-C12) arranged either side of a slab of 342 water molecules approximately 30 Åthick. The surfactant chains are treated with rigid bonds and the water molecules are treated as rigid bodies. The TAB headgroup has fractional charges summing to +1 (the bromide ion has charge -1). The Ewald sum handles the electrostatic calculations. The short range forces are taken from the Dreiding force field.

5.1.1.10 Test Case 10: DNA strand in water

This system consists of a strand of DNA 1260 atoms in length in a solution of 706 (SPC) water molecules. The DNA is aligned in the Z-direction and *hexagonal prism* periodic boundary conditions applied. The electrostatic interactions are calculated using the Smooth Particle Mesh Ewald method. Note that the system has a strong overall negative charge which is strongly anisotropic in distribution. The short range forces are taken from the Dreiding force field, and constraints are used for all covalent bonds. For simplicity H-bonds are treated as harmonic bonds with an equilibrium bondlength of 1.724 Å.

5.1.2 Benchmark Cases

These represent rather larger test cases for DL_POLY_2 that are also suitable for benchmarking the code on large scale computers. They have been selected to show fairly the the capabilities and limitations of the code.

5.1.2.1 Benchmark 1

Simulation of metallic aluminium at 300K using a Sutton-Chen density dependent potential. The system is comprised of 19652 identical atoms. The simulation runs on 16 to 512 processors only.

5.1.2.2 Benchmark 2

Simulation of a 15-peptide in 1247 water molecules. This was designed as an AMBER comparison. The system consists of 3993 atoms in all and runs on 8-512 processors. It uses neutral group electrostatics and rigid bond constraints and is one of the smallest benchmarks in the set.

5.1.2.3 Benchmark 3

Simulation of the enzyme transferrin in 8102 water molecules. The simulation makes use of neutral group electrostatics and rigid bond constraints. The system is 27539 atoms and runs on 8-512 processors.

5.1.2.4 Benchmark 4

Simulation of a sodium chloride melt with Ewald sum electrostatics and a multiple timestep algorithm to enhance performance. The system is comprised of 27000 atoms and runs on 8-512 processors.

5.1.2.5 Benchmark 5

Simulation of a sodium-potassium disilicate glass. Uses Ewald sum electrostatics, a multiple timestep algorithm and a three-body valence angle potentials to support the silicate structure. It also using tabluated two-body potentials stored in the file TABLE. The system is comprised of 8640 atoms and runs on 16-512 processors.

5.1.2.6 Benchmark 6

Simulation of a potassium-valinomycin complex in 1223 water molecules using an adapted AMBER forcefield and truncated octahedral periodic boundary conditions. The system size is 3838 atoms and runs on 16-512 processors.

5.1.2.7 Benchmark 7

Simulation of gramicidin A molecule in 4012 water molecules using neutral group electrostatics. The system is comprised of 12390 atoms and runs on 8-512 processors. This example was provided by Lewis Whitehead at the University of Southampton.

5.1.2.8 Benchmark 8

Simulation of an isolated magnesium oxide microcrystal comprised of 5416 atoms originally in the shape of a truncated octahedron. Uses full coulombic potential. Runs on 16-512 processors.

5.1.2.9 Benchmark 9

Simulation of a model membrane with 196 41-unit membrane chains, 8 valinomycin molecules and 3144 water molecules using an adapted AMBER potential, multiple timestep algorithm and Ewald sum electrostatics. The system is comprised of 18866 atoms and runs on 8-512 processors.

Chapter 6

DL_POLY_2 Utilities

Scope of Chapter

This chapter describes the more important utility programs and subroutines of DL_POLY_2 , found in the sub-directory *utility*. A more complete description of the sub-directory contents is to be found in the DL_POLY_2 Reference Manual.

6.1 Miscellaneous Utilities

6.1.1 PARSET

6.1.1.1 Header records

```
      program parset

c
c*********************************************************************
c
c     dl_poly utility program to prepare the dl_params.inc file
c     for specific dl_poly applications
c
c     author - w.smith, t.forester jan 1995
c     copyright daresbury laboratory 1995
c
c*********************************************************************
c
```

6.1.1.2 Function

PARSET is designed to provide estimates of the FORTRAN parameters (e.g. array dimensions) required by versions of DL_POLY_2 prior to 2.11 to simulate a given system i.e. those required for the dl_params.inc file. By scanning the CONTROL, FIELD and CONFIG files of the intended simulation PARSET is able to calculate estimates of minimum parameters needed. The calculated parameters are written into a file: *new_params.inc*, which is FORTRAN compatible. Once this has been renamed DL_PARAMS.INC, it can be used directly when DL_POLY_2 is compiled. Use of PARSET is strongly recommended as a means of reducing the effort needed to create a working DL_POLY_2 executable.

Note. PARSET is required only for versions of DL_POLY_2 prior to version 2.11.

6.1.1.3 Dependencies

- None (PARSET is self contained.)

6.1.1.4 Parameters

- None (There are no internal arrays.)

6.1.1.5 Input

Interactive:

record 1:

`min_nodes`	integer	minimum number of processing nodes

record 2:

`max_nodes`	integer	maximum number of processing nodes

Data Files:

input.data:

CONTROL	Standard DL_POLY_2 CONTROL input file
CONFIG	Standard DL_POLY_2 CONFIG input file
FIELD	Standard DL_POLY_2 FIELD input file
TABLE	Standard DL_POLY_2 TABLE input file (optional)

output.data:

new_params.inc	New parameters include file

6.1.1.6 Comments

PARSET does not undertake any error checking of the CONTROL, FIELD and CONFIG files. Any errors in these files will result in an incorrect parameters file. It must also be recognised that for some of the parameters, there is no straightforward formula for calculating suitable values from the input files. In these cases the parameters produced represent a reasonable estimate only. Fortunately, these cases are few in number and as a rule PARSET will significantly reduce the time needed to prepare a working version of DL_POLY_2 .

It is useful to prepare the input files assuming the largest simulation you are likely to attempt on a given system. This will generate the largest executable necessary to prevent you having to recompile the code in the course of your study.

6.1.2 Useful Macros

6.1.2.1 Macros

Macros are simple executable files containing standard unix commands. A number of the are supplied with DL_POLY and are found in the *execute* sub-directory. The available macros are as follows.

- *cleanup*
- *copy*
- *gopoly*
- *select*
- *store*

The function of each of these is described below. It is worth noting that most of these functions can be perfomed by the DL_POLY_2 GUI [20].

6.1.2.2 *cleanup*

cleanup removes several standard data files from the *execute* sub-directory. It contains the unix commands:

```
rm OUTPUT REVCON REVOLD STATIS REVIVE gopoly.*
```

and removes the files OUTPUT, REVCON, REVOLD, STATIS, REVIVE and gopoly.* (all variants). It is useful for cleaning the sub-directory up after a run. (Useful data should be stored elsewhere however!)

6.1.2.3 *copy*

copy invokes the unix commands:

```
mv CONFIG CONFIG.OLD
mv REVCON CONFIG
mv REVIVE REVOLD
```

which collectively prepare the DL_POLY files in the *execute* sub-directory for the continuation of a simulation. It is always a good idea to store these files elsewhere in addition to using this macro.

6.1.2.4 *gopoly*

gopoly is used to submit a DL_POLY job to the Daresbury IBM SP/2, which operates a LOADLEVELLER job queuing system. It invokes the following script.

```
#@ min_processors = 4
#@ max_processors = 4
#@ job_type = parallel
#@ requirements = (Adapter == "hps_ip") && ( Pool == 2)
#@ executable = /usr/bin/poe
#@ cpu_limit = 00:10:00
#@ arguments = ~/dl_poly_2.10/execute/DLPOLY.X -euilib ip
#@ output = gopoly.o
#@ error = gopoly.e
#@ class = dev
#@ queue
```

Using LOADLEVELLER, the job is submitted by the unix command:

llsubmit gopoly

where *llsubmit* is a local command for submission to the SP/2. The number of required nodes and the job time are indicated in the above script.

6.1.2.5 *select*

select is a macro enabling easy selection of one of the test cases. It invokes the unix commands:

```
cp ../data/TEST$1/CONTROL CONTROL
cp ../data/TEST$1/FIELD   FIELD
cp ../data/TEST$1/CONFIG  CONFIG
```

select requires one argument (an integer) to be specified:

select n

where *n* is test case number, which ranges from 1 to 10.

This macro sets up the required input files in the *execute* sub-directory to run the *n*-th test case.

6.1.2.6 *store*

The *store* macro provides a convenient way of moving data back from the *execute* sub-directory to the *data* sub-directory. It invokes the unix commands:

```
mkdir ../data/TEST$1
mv OUTPUT ../data/TEST$1/OUTPUT
mv REVCON ../data/TEST$1/REVCON
mv STATIS ../data/TEST$1/STATIS
mv REVIVE ../data/TEST$1/REVIVE
mv RDFDAT ../data/TEST$1/RDFDAT
mv ZDNDAT ../data/TEST$1/ZDNDAT
chmod 400 ../data/TEST$1/*
```

which first creates a new DL_POLY *data/TEST.*. sub-directory and then moves the standard DL_POLY output data files into it.

store requires one argument:

store n

where *n* is a unique string or number to label the output data in the *data/TESTn* sub-directory.

Note that *store* sets the file access to read-only. This is to prevent the *store* macro overwriting existing data without your knowledge.

Chapter 7

DL_POLY_2 Subroutines and Functions

Scope of Chapter

This chapter describes all the subroutines of DL_POLY_2 to be found in the *source* subdirectory. A fuller description of the contents of the *source* sub-directory is available in the DL_POLY_2 Reference Manual.

7.1 Subroutine and Function Specifications

7.1.1 DL_PARAMS.INC: The DL_POLY Parameters (Include) File

7.1.1.1 Header

```
c*********************************************************************
c
c     dl_poly insert file specifying array sizes for the
c     entire package
c
c     copyright - daresbury laboratory 1994
c     authors - w. smith & t. forester november  1994.
c
c
c     note the following internal units apply everywhere
c
c     unit of time      (to)    =          1 x 10**(-12) seconds
c     unit of length    (lo)    =          1 x 10**(-10) metres
c     unit of mass      (mo)    = 1.6605402  x 10**(-27) kilograms
c     unit of charge    (qo)    = 1.60217733 x 10**(-19) coulombs
c     unit of energy    (Eo)    = 1.6605402  x 10**(-23) joules
c     unit of pressure  (Po)    = 1.6605402  x 10**(  7) pascals
c                               = 163.842151             atmospheres
c
c*********************************************************************
c
```

7.1.1.2 Function

The DL_POLY_2 parameters file for version 2.10 (and earlier) contains all the parameters defining the arrays dimensions of DL_POLY_2 plus the fundamental constants and conversion factors. In the include file for version 2.11 (and after) the bulk of these parameters take the form of FORTRAN integer variables, which are stored in the COMMON block /params/. Apart from this difference, the meaning and function of the parameters is the same. The DL_PARAMS.INC file is included in all relevant subroutines at compile time.

7.1.1.3 The Parameters and their Function

In the following table the values of parameters that are dependent on the simulated system are given as *variable*. Some parameter values may be derived from others, and a simple formula is given. An example of a working parameters file can be found in the *source* subdirectory.

parameter	**value**	**function**

boltz	0.831451115	boltzmann constant in internal units
kmaxb	*variable*	max reciprocal space vector index (b direction)
kmaxc	*variable*	max reciprocal space vector index (c direction)
minnode	*variable* $\geq$ 1	min number of nodes for code execution
msatms	mxatms/minnode+1	max number of atoms in working arrays
msbad	max(mxbond,mxangl, mxdihd,mxteth,mxinv, mxshl)	max size of working arrays for bond, angle, dihedral, tether,inversion and shell routines
msgrp	mxgrp/minnode+1	max number of rigid groups per node
mslst	mxatms/minnode+1	max number of atoms in Verlet test arrays
mspmf	*variable*	max number of potential of mean force constraints per node
msteth	*variable*	max number of tethered atoms per node
mx2tbp	*variable le* mxvdw	array dimension of 3-body potential parameters
mx3fbp	*variable*	array dimension of 4-body potential parameters
mxangl	*variable*	max number of bond angles on a node
mxatms	*variable*	max number of atoms in system
mxbond	*variable*	max number of chemical bonds on a node
mxbuff	max(6*mxatms, 8*(mxcons+1), 8*(mxgrp+1), mxnstk*mxstak, mxebuf, mxgrid)	max dimension of atomic transfer buffer
mxcell	*variable*	max number of link cells in system
mxcons	*variable*	max number of constraint bonds on a node
mxdihd	*variable*	max number of torsion angles on a node
mxewld	msatms or mxatms	max of array elements in EWALD1(A) work arrays
mxexcl	*variable*	max number of excluded interactions per atom
mxfbd	*variable*	max number of defined 4-body force potentials
mxfld	10	max number of external field parameters
mxgatm	*variable* $\leq$ mxatms	max number of sites in rigid units
mxgrid	*variable*	max number of grid points in potential arrays
mxgrp	*variable*	max number of rigid body units in system
mxinv	*variable*	max number of inversion potentials per node
mxlist	*variable*	max number of atoms in verlet list
mxlshp	2*mxcons	max dimension of shape routine transfer array
mxmols	*variable*	max number of molecules
mxneut	*variable*	max number of neutral groups + 1
mxngp	*variable* $\geq$ *3*	max number of sites in a rigid unit
mxnstk	mxsvdw+45	max number of stacked variables
mxpang	4	max number of angle potential parameters
mxpbnd	4	max number of bond potential parameters
mxpdih	5	max number of dihedral potential parameters
mxpfbp	3	max number of 4-body potential parameters

mxpinv	2	max number of inversion potential parameters
mxpmf	*variable* ≤mxatms	number of atoms in potential of mean force constraints
mxproc	*variable*	max number of nodes (used in parallel constraint algorithm)
mxptbp	mxpang+1	max number of 3-body potential parameters
mxpvdw	5	max number of van der Waals potential parameters
mxquat	*variable*	max iterations in quaternion integration
mxrdf	*variable*	number of tabulation points for radial distribution functions
mxshak	*variable*	max number of iterations in shake algorithm
mxshl	*vaiable*	max number of core-shell units
mxsite	*variable*	max number of molecular sites
mxspmf	*variable*	max number sites to define pmf units
mxstak	*variable*	dimension of stack arrays for rolling averages
mxsvdw	*variable*	max number of different types of sites for pair potentials
mxtang	*variable*	max number of different bond angle potentials
mxtbnd	*variable*	max number of chemical bond potentials
mxtbp	mxvdw*mxsvdw	max number of 3-body potentials
mxtcon	*variable*	max number of specified bondlength constraints
mxtdih	*variable*	max number of different dihedral potentials
mxteth	*variable*	max number of tethered atom potentials
mxtinv	*variable*	max number of inversion potentials
mxtmls	*variable*	max number of molecule types
mxtshl	*variable*	max number of core-shell unit types
mxungp	*variable*	max number unique rigid body units
mxvdw	((mxsvdw+1)* mxsvdw)/2	max number of different pair potentials (×2 if Sutton-Chen potentials used)
mxxdf	max(mxlist,msatms, mxcons,mxn1*mxn1* (mxneut+1)/2)	max number of atoms in xdf,ydf and zdf arrays (mxn1 is number of sites in largest neutral group)
nconf	8	configuration file input channel
ndump	*variable*	data dumping interval in event of system crash
nfield	7	force field input channel
nhist	21	trajectory history file channel
nrdfdt	24	output channel for RDF data
nread	5	main input channel
nrest	22	output channel accumulators restart dump file
nrite	6	main output channel
nstats	20	statistical data file output channel
ntable	23	tabulated potentials file input channel
nzdfdt	25	output channel for Z-density data file
pi	3.141592653589793	π

`prsunt`	1.63842151d-1	pressure conversion factor
`r4pie0`	138935.4835	electrostatic conversion factor i.e. (unit(charge)**2/(4 pi eps0 unit(length))/ unit(energy)
`sqrpi`	1.7724538509055159	square root of π

7.1.1.4 Comments

1. A working version of the parameters file (for DL_POLY_2 versions prior to 2.11), for any given application, can be constructed with the aid of the utility program PARSET see section 6.1.1 of the DL_POLY_2 Reference Manual.

2. Many of the above parameters refer to array dimensions. If the application does not use the associated functionality, these parameters may be set to 1. e.g. `mxtang` and `mxangl` may both be set to 1 if the simulation does not require bond angles.

3. Any changes made to the parameters file requires the entire program to be recompiled. (The *build* directory contains example makefiles which do this automatically.)

4. The parameters to found in the /params/ COMMON block (versions 2.11 and above) may be determined from the following FORTRAN extract, taken from the DL_PARAMS.INC file. The variables appearing have the same meaning as the parameters described above.

```
c     array allocation parameters (set by subroutine parset)

      common/params/kmaxa,kmaxb,kmaxc,minnode,msatms,msbad,msgrp,
     x      mspmf,msteth,mxangl,mxatms,mxbond,mxbuff,mxcell,
     x      mxcons,mxdihd,mxewld,mxexcl,mxfbp,mxfld,mxgatm,mxgrid,
     x      mxgrp,mxinv,mxlist,mxlshp,mxneut,mxngp,mxnstk,mxpang,
     x      mxpbnd,mxpdih,mxpfbp,mxpinv,mxpmf,mxproc,mxptbp,mxpvdw,
     x      mxrdf,mxshl,mxsite,mxspmf,mxstak,mxsvdw,mxtang,mxtbnd,
     x      mxtbp,mxtcon,mxtdih,mxteth,mxtinv,mxtmls,mxtshl,mxungp,
     x      mxvdw,mxxdf,mx2tbp,mx3fbp,mxebuf,mxquat,mxshak
```

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Appendix A

The DL_POLY_2 Makefile

```
# Master makefile for DL_POLY_2.0
# Author: W. Smith November 1999
# With DPP tool by J. Geronowicz
# Original by T. Forester 1995
#
#     $Author: wl $
#     $Date: 2000/01/17 17:01:09 $
#     $Revision: 1.8 $
#     $State: Exp $

# Define default settings

#====================================================================

FFTW_LIBRARY = ""
BINROOT = ../execute
CC  = cc
DPP = ./dpp
EX = DLPOLY.X
EXE = $(BINROOT)/$(EX)
FC=undefined
PVM_EX=\'$(EX)\'
SHELL=/bin/sh
STRESS=STRESS
TYPE=3pt

# Define object files

#====================================================================
```

```
OBJ_ALL = angfrc.o bndfrc.o cfgscan.o corshl.o coul0.o coul4.o \
coul2.o coul3.o conscan.o dblstr.o dcell.o diffsn0.o \
diffsn1.o dlpoly.o duni.o error.o ewald1.o ewald3.o \
exclude.o exclude_atom.o fldscan.o exclude_link.o \
exitcomms.o extnfld.o fbpfrc.o fcap.o forces.o freeze.o gauss.o \
gdsum.o getrec.o gimax.o gisum.o gstate.o images.o initcomms.o \
intlist.o intstr.o invert.o invfrc.o jacobi.o lowcase.o lrcmetal.o \
lrcorrect.o machine.o merge.o merge1.o merge4.o multiple.o  \
multiple_nsq.o npt_b1.o npt_b3.o parset.o npt_h1.o npt_h3.o nve_1.o \
nvt_b1.o nvt_e1.o nvt_h1.o parlst_nsq.o parlink.o parlst.o passcon.o \
passpmf.o pmf_1.o pmf_shake.o primlst.o quench.o rdf0.o rdf1.o \
rdshake_1.o result.o revive.o scdens.o shellsort.o shlfrc.o \
shlmerge.o shlqnch.o shmove.o simdef.o splice.o static.o strip.o \
strucopt.o sysdef.o sysgen.o systemp.o sysbook.o sysinit.o \
tethfrc.o thbfrc.o timchk.o traject.o vertest.o vscaleg.o \
warning.o xscale.o zden0.o zden1.o

OBJ_SPME = bspcoe.o bspgen.o cpy_rtc.o ele_prd.o ewald_spme.o \
 scl_csum.o set_block.o spl_cexp.o spme_for.o

OBJ_NEU = coul0neu.o coul2neu.o coul3neu.o excludeneu.o forcesneu.o \
multipleneu.o neutlst.o parneulst.o prneulst.o \
parlinkneu.o rdf0neu.o

OBJ_RIG = nptq_b1.o nptq_b2.o nptq_b3.o nptq_b4.o nptq_h1.o nptq_h2.o \
nptq_h3.o nptq_h4.o nveq_1.o nveq_2.o nvtq_b1.o nvtq_b2.o \
nvtq_h1.o nvtq_h2.o passquat.o qshake.o quatbook.o quatqnch.o

OBJ_RRR = denloc.o dihfrc.o erfcgen.o ewald2.o ewald4.o forgen.o \
fortab.o metgen.o srfrce.o srfrceneu.o suttchen.o

OBJ_4PT = denloc_4pt.o dihfrc_4pt.o erfcgen.o ewald2_4pt.o ewald4_4pt.o \
forgen.o fortab.o metgen.o srfrce_4pt.o srfrceneu_4pt.o \
suttchen_4pt.o

OBJ_RSQ = denloc_rsq.o dihfrc_rsq.o erfcgen_rsq.o ewald2_rsq.o ewald4_rsq.o \
forgen_rsq.o fortab_rsq.o metgen_rsq.o srfrce_rsq.o srfrceneu_rsq.o\
suttchen_rsq.o

OBJ_EXT = crecv.o csend.o gsync.o mynode.o nodedim.o numnodes.o

TIMER = etime.o

# Define targets
```

```
#=====================================================================
all:
@echo "Error - please specify a target machine!"
@echo "Permissible targets for this Makefile are:"
@echo "                                              "
@echo "alpha-linux"
@echo "alpha-linux-fftw"
@echo "beowulf-absoft"
@echo "cray-t3e"
@echo "cray-t3e-serial"
@echo "cray-t3e-totalview"
@echo "dec-alpha"
@echo "dec-alpha-ev6"
@echo "exemplar"
@echo "hitachi-sr2201"
@echo "hp"
@echo "hp-c240"
@echo "intel"
@echo "linux"
@echo "pentium-absoft"
@echo "pentium-portland"
@echo "rs6k"
@echo "rs6k-pwr3"
@echo "sg10k"
@echo "sg10k-fftw"
@echo "sg2-r5k"
@echo "sg2k"
@echo "sg2k-i6.5"
@echo "sg2k-shmem"
@echo "sg8k-mpi"
@echo "sg8k-mpi-f"
@echo "sp2-mpi"
@echo "sp2-mpi-debug"
@echo "sp2-mpi-fftw"
@echo "sun"
@echo "sun-ultra"
@echo "         "
@echo "Please examine Makefile for details"

# system specific targets follow :

#================== IBM SP2 version ====================================
sp2-mpi: dpp
```

```
cp /usr/lpp/ppe.poe/include/mpif.h mpif.h
$(MAKE) FC=mpxlf FFLAGS="-c -NS2048 -qarch=pwr2 -qnosave" \
CPFLAGS="-D$(STRESS) -DMPI -DESSL -D'POINTER=integer'" intlist.o
$(MAKE) LD="mpxlf -o" LDFLAGS="-lesslp2" FC=mpxlf \
FFLAGS="-c -O3 -NS2048  -qarch=pwr2 -qnosave" \
CPFLAGS="-D$(STRESS) -DMPI -DESSL -D'POINTER=integer'" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#================= IBM SP2 debug version ============================
sp2-mpi-debug: dpp
cp /usr/lpp/ppe.poe/include/mpif.h mpif.h
$(MAKE) LD="mpxlf -o" LDFLAGS="-lesslp2" FC=mpxlf \
FFLAGS="-g -c -C -NS2048  -qarch=pwr2 -qnosave"  \
CPFLAGS="-D$(STRESS) -DMPI -DESSL -D'POINTER=integer'" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#================= IBM SP2 FFTW version ============================
sp2-mpi-fftw: dpp
cp /usr/lpp/ppe.poe/include/mpif.h mpif.h
$(MAKE) FC=mpxlf FFLAGS="-c -NS2048 -qarch=pwr2 -qnosave" \
CPFLAGS="-D$(STRESS) -DMPI -D'POINTER=integer' -DFFTW
$(MAKE) LD="mpxlf -o" LDFLAGS="-lesslp2 -lfftw -lrfftw -L$(FFTW_LIBRARY)" \
FC=mpxlf FFLAGS="-c -O3 -NS2048  -qarch=pwr2 -qnosave" \
CPFLAGS="-D$(STRESS) -DMPI -D'POINTER=integer' -DFFTW -DESSL" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#===== Cray t3e (Manchester) ========================================
cray-t3e: dpp
cp /opt/ctl/mpt/mpt/include/mpif.h mpif.h
$(MAKE) FC="f90" FFLAGS="-c -dp -lmpi" \
CPFLAGS="-Wp'-DCRAY -DCRAY_T3D -D'POINTER=integer' -DSHMEM -D$(STRESS) -P'" \
lowcase.o
$(MAKE) LD="f90 -o" FC="f90" FFLAGS="-c -dp -lmpi" LDFLAGS="-lmpi" \
CPFLAGS="-Wp'-DCRAY -DCRAY_T3D -D'POINTER=integer' \
-DSHMEM -D$(STRESS) -P'"  TIMER="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#===== Cray t3e (Manchester) with totalview flags ====================
cray-t3e-totalview: dpp
cp /opt/ctl/mpt/mpt/include/mpif.h mpif.h
$(MAKE) FC="f90" FFLAGS="-c -dp -lmpi -g -X8" \
CPFLAGS="-Wp'-DCRAY -DCRAY_T3D -D'POINTER=integer' -DSHMEM -D$(STRESS) -P'" \
lowcase.o
$(MAKE) LD="f90 -o" FC="f90" FFLAGS="-c -dp -lmpi  -g -X8" \
LDFLAGS="-lmpi -g -X8" \
```

```
CPFLAGS="-Wp'-DCRAY -DCRAY_T3D -D'POINTER=integer' \
-DSHMEM -D$(STRESS) -P'" TIMER="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========== Cray t3e (serial) ============================================
cray-t3e-serial: dpp
$(MAKE) LD="f90 -o" LDFLAGS="" FC=f90 \
FFLAGS="-c -dp -O3,aggress,unroll2,nojump" TIMER="" \
CPFLAGS="-D$(STRESS) -DSERIAL -P -D'POINTER=intger'" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========= Linux (no SPME) ================================================
linux: dpp
$(MAKE) FC=f77 FFLAGS="-c" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" qshake.o
$(MAKE) LD="f77 -o" LDFLAGS="" FC=f77 FFLAGS="-c -g" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" \
OBJ_SPME="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========== DEC Alpha (no SPME) ===========================================
dec-alpha: dpp
$(MAKE) LD="f90 -o" FC=f90 FFLAGS="-c -fast" \
LDFLAGS="-math_library fast -assume noaccuracy_sensitive" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer*8'" \
TIMER="" OBJ_SPME="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========== DEC Alpha ev6 (no SPME) =======================================
dec-alpha-ev6: dpp
$(MAKE) LD="f90 -o" FC=f90 FFLAGS="-c -arch ev6 -fast" \
LDFLAGS="-arch ev6 -math_library fast -assume noaccuracy_sensitive"  \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer*8'" \
TIMER="" OBJ_SPME="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#======== Alpha Linux (no SPME) ===========================================
alpha-linux: dpp
$(MAKE) FC=fort FFLAGS="-c -O -fast" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer*8'" qshake.o
$(MAKE) FC=fort LD="fort -o" FFLAGS="-c -O -fast" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer*8' \
LDFLAGS="" OBJ_SPME="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#======== Alpha Linux (plus SPME via FFTW) ================================
alpha-linux-fftw: dpp
$(MAKE) FC=fort FFLAGS="-c -O -fast" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer*8'" qshake.o
```

```
$(MAKE) FC=fort LD="fort -o" FFLAGS="-c -O -fast" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer*8' -DFFTW" \
LDFLAGS="-lfftw -lrfftw -L$(FFTW_LIBRARY)" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#================== HP Workstation version (no SPME) ==================
hp: dpp
$(MAKE) FC=f77 FFLAGS="-c" CPFLAGS="-D$(STRESS) -DSERIAL
-D'POINTER=integer'" qshake.o
$(MAKE) LD="f77 -o" LDFLAGS="" FC=f77 FFLAGS="-c -O" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" \
OBJ_SPME="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========= Convex/HP exemplar (serial) (no SPME) ======================
exemplar: dpp
$(MAKE) LD="f90 -o" LDFLAGS=""  FC=f90 FFLAGS=" -c +ppu +O2 +DA2.0" \
CPFLAGS="-D$(STRESS) -DSERIAL" -D'POINTER-integer' \
OBJ_SPME="" TIMER="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========= HP PA 9000 / C240 (serial) (no SPME) ========================
hp-c240: dpp
$(MAKE) LD="f90 -o" LDFLAGS=  FC=f90 FFLAGS=" -c +ppu +O2 +DA2.0" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" \
OBJ_SPME="" TIMER="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#============= IBM (AIX) Workstation version (no SPME) ==================
aix: dpp
$(MAKE) FC=mpxlf FFLAGS="-c -NS2048 -qarch=pwr2 -qnosave" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" intlist.o
$(MAKE) LD="xlf -o" LDFLAGS="" FC=xlf FFLAGS="-c -O3 -NS2048 -qarch=pwr2 -qnosave"\
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" \
OBJ_SPME="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========= RS/6000 P2SC (serial) (no SPME) ==============================
rs6k: dpp
$(MAKE) LD="xlf -o" LDFLAGS=  FC=xlf \
FFLAGS="-c -O -qarch=pwr2 -qtune=pwr2" TIMER="" OBJ_SPME=""\
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========= RS/6000 Power3 (serial) ======================================
rs6k-pwr3: dpp
$(MAKE) LD="xlf -o" LDFLAGS="-L/usr/local/lib -lmass -lessl"  \
FC=xlf FFLAGS="-c -O -qnosave -qarch=pwr3" TIMER="" \
CPFLAGS="-D$(STRESS) -DSERIAL" -DESSL -D'POINTER=integer' \
```

```
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========== PentiumII (absoft) (serial) (no SPME) ======================
pentium-absoft: dpp
$(MAKE) LD="/usr/bin/f90 -o" LDFLAGS="-lfio" TIMER="" OBJ_SPME=""  \
FC=/usr/bin/f90 FFLAGS="-c -YEXT_NAMES=LCS -B108 -B100 -O" \
CPFLAGS="-D$(STRESS) -DSERIAL -P -D'POINTER=integer' " \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========== PentiumII (portland) (serial) (no SPME) =====================
pentium-portland: dpp
$(MAKE) LD="/usr/local/pgi/linux86/bin/pgf90 -o" LDFLAGS="" \
FC=/usr/local/pgi/linux86/bin/pgf90 FFLAGS="-c -O -Mdalign" \
CPFLAGS="-D$(STRESS) -DSERIAL -P -D'POINTER=integer'" \
TIMER="" OBJ_SPME="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#======== Hitachi SR2201 Multiprocessor (no SPME) =======================
hitachi-sr2201: dpp
cp /usr/include/mpif.h mpif.h
$(MAKE) FC=xf90 \
FFLAGS="-c -W0,'form(fixed),opt(o(3)),langlvl(save(0))' -s,TRACE" \
CPFLAGS="-D$(STRESS) -DMPI -D'POINTER=integer'" intlist.o
$(MAKE) LDFLAGS="" LDLIBS="-lfmpi -lmpi" LD="xf90 -o" FC=xf90 \
FFLAGS="-c -W0, 'form(fixed),opt(o(3)),langlvl(save(0))' -s,TRACE" \
CC=xcc TIMER="" CPFLAGS="-D$(STRESS) -DMPI
-D'POINTER=integer'" OBJ_SPME="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#======== Intel (no SPME) ================================================
intel: dpp
$(MAKE) FC=if77 LD="if77 -o" LDFLAGS="-node -glob -Knoieee" \
FFLAGS="-c -O2" CPFLAGS="-D$(STRESS) -DINTEL \
-D'POINTER=integer'" OBJ_SPME="" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#======== Silicon Graphics 10000 Worskstation ============================
sg10k: dpp
$(MAKE) LD="f90 -o" LDFLAGS="-lscs" \
FC=f90 FFLAGS="-c -O2 -OPT:Olimit=0 -lscs" TIMER="" \
CPFLAGS="-DCRAY -D$(STRESS) -DSERIAL -D'POINTER=integer'" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#======== Silicon Graphics 10000 Worskstation (SPME via FFTW) ===========
sg10k-fftw: dpp
$(MAKE) LD="f90 -o" LDFLAGS="-lscs -lfftw -lrfftw -L$(FFTW_LIBRARY)" \
FC=f90 FFLAGS="-c -O2 -OPT:Olimit=0 -lscs" TIMER="" \
```

```
CPFLAGS="-DCRAY -D$(STRESS) -DSERIAL -D'POINTER=integer' -DFFTW" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========= Silicon Graphics 8000 (parallel) ==========================
sg8k-mpi: dpp
cp /usr/include/mpif.h mpif.h
$(MAKE) LD="f90 -O3 -64 -o" FC=f90 LDFLAGS="-lmpi" TIMER="" \
FFLAGS="-c -O3  -64 " CPFLAGS="-D$(STRESS) -DMPI \
-DCRAY -D'POINTER=integer'" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========= Silicon Graphics 8000 (parallel) ==========================
sg8k-mpi-f: dpp
cp /usr/include/mpif.h mpif.h
$(MAKE) LD="f90 -Ofast -64 -o" FC=f90 LDFLAGS="-lmpi" TIMER=""\
FFLAGS="-c -Ofast  -64" CPFLAGS="-D$(STRESS) -DMPI \
-DCRAY -D'POINTER=integer'" EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#======= Silicon Graphics Origin 2000 (parallel/SHMEM) ===============
sg2k-shmem: dpp
cp /usr/include/mpif.h mpif.h
$(MAKE) LD="f90 -o" FC=f90 \
FFLAGS="-c -64 -mips4 -Ofast=ip27 -IPA -OPT:Olimit=0 " \
LDFLAGS="-64 -mips4 -Ofast=ip27 -IPA -OPT:Olimit=0 -lsma -lmpi -lblas" \
OBJ_EXT="gsync.o mynode.o nodedim.o numnodes.o" TIMER="" \
CPFLAGS="-DMPI -D$(STRESS) -DSGI_O2K -DCRAY -D'POINTER=integer'" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========= Silicon Graphics Origin 2000 (serial) (no SPME) ===========
sg2k: dpp
$(MAKE) LD="f90 -o" LDFLAGS="-n32 -mips4"  FC=f90 \
FFLAGS="-c -O3 -G 0 -mips4 -r10000 -c -r8 -n32" \
TIMER="" OBJ_SPME="" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" \
CFLAGS="-c -O3 -n32 -mips4 -r10000" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#=== Silicon Graphics Origin 2000 (serial, Irix 6.5) (no SPME) =======
sg2k-i6.5: dpp
$(MAKE) LD="f90 -o" LDFLAGS="-n32 -mips4 -IPA"  \
FC=f90 FFLAGS="-c -n32 -mips4 -Ofast=ip27 -LNO:fusion=2" \
TIMER="" OBJ_SPME="" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" \
CFLAGS="-c -O3 -n32 -mips4 -r10000" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)
```

```
#=== Silicon Graphics O2 R5k (serial) (no SPME) ======================
sg2-r5k: dpp
$(MAKE) LD="f90 -o" LDFLAGS="-n32 -mips4"  \
FC=f90 FFLAGS="-c -O3 -G 0 -mips4 -r5000 -c -r8 -n32" \
TIMER="" OBJ_SPME="" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" \
CFLAGS="-c -O3 -n32 -mips4 -r5000" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========= SUN Workstation version (no SPME) ========================
sun: dpp
$(MAKE) LD="f77 -o" LDFLAGS="" FC=f77 FFLAGS="-c -O2" \
TIMER="" OBJ_SPME="" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#======== Sun Ultra-2 (serial) (no SPME) ============================
sun-ultra: dpp
$(MAKE) LD="/opt/SUNWspro/bin/f90 -o" LDFLAGS=  \
FC=/opt/SUNWspro/bin/f90 \
FFLAGS="-c -fnonstd -xarch=v8plusa -xchip=ultra -O2 -libmil -dalign" \
TIMER="" OBJ_SPME="" \
CPFLAGS="-D$(STRESS) -DSERIAL -D'POINTER=integer'" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#========= Daresbury Beowulf (Absoft compiler) (no SPME)==============
beowulf-absoft: dpp
cp /usr/local/lam-6.2/h/mpif.h mpif.h
$(MAKE) LD="/usr/bin/f90 -o" \
LDFLAGS="-L/home/kcm/mpich-absoft/mpich/lib/LINUX/ch_p4/ -lmpich" \
FC=/usr/bin/f90 FFLAGS="-c -O -B100" TIMER="" OBJ_SPME="" \
CPFLAGS="-D$(STRESS) -DMPI -P -D'POINTER=integer' \
-I/home/kcm/mpich-absoft/mpich/include" \
EX=$(EX) BINROOT=$(BINROOT) $(TYPE)

#=====================================================================
# Interpolation tables options

# Default code. Force tables interpolation in r-space 3pt interpolation
3pt: check $(OBJ_ALL) $(OBJ_RRR) $(OBJ_NEU) $(OBJ_RIG) $(OBJ_EXT) $(TIMER) $(OBJ_SPME)
$(LD) $(EXE) $(OBJ_ALL) $(OBJ_RRR) $(OBJ_NEU) $(OBJ_RIG) $(OBJ_EXT) $(TIMER) \
$(LDFLAGS) $(LDLIBS) $(OBJ_SPME)
```

```
# Force tables interpolation in r-space, 4pt interpolation
4pt: check $(OBJ_ALL) $(OBJ_4PT) $(OBJ_NEU) $(OBJ_RIG) $(OBJ_EXT) $(TIMER) $(OBJ_SPME)
$(LD) $(EXE) $(OBJ_ALL) $(OBJ_4PT) $(OBJ_NEU) $(OBJ_RIG) $(OBJ_EXT) $(TIMER) \
$(LDFLAGS) $(LDLIBS) $(OBJ_SPME)

# Force tables interpolation in  r-squared
rsq: check $(OBJ_ALL) $(OBJ_RSQ)  $(OBJ_NEU) $(OBJ_RIG) $(OBJ_EXT) $(TIMER) $(OBJ_SPME)
$(LD) $(EXE) $(OBJ_ALL) $(OBJ_RSQ) $(OBJ_NEU) $(OBJ_RIG) $(OBJ_EXT) $(TIMER) \
$(LDFLAGS) $(LDLIBS) $(OBJ_SPME)

#=====================================================================
# Check that a machine has been specified
check:
@if test $(FC) = "undefined";\
then echo "You must specify a target machine!"; \
exit 99;\
fi

#=====================================================================
# Clean up the source directory
clean:
rm -f $(OBJ_ALL) $(OBJ_RRR) $(OBJ_EXT) $(OBJ_NEU) \
$(OBJ_RIG) $(TIMER) $(OBJ_SPME) $(OBJ_4PT) $(OBJ_RSQ) \
*.tmp.f mpif.h

#=====================================================================
# Compile preprocessor code
dpp: dpp.c
$(CC) dpp.c -o dpp

#=====================================================================
# Declare dependencies : c preprocess all .f files
.f.o:
$(DPP) $(CPFLAGS)  $*.f > $*.tmp.f
$(FC) $(FFLAGS) $*.tmp.f
mv $*.tmp.o $*.o

.c.o:
$(CC) -c $*.c

#=====================================================================
# Declare dependency on parameters file

$(OBJ_ALL): dl_params.inc
```

```
$(OBJ_RRR): dl_params.inc
$(OBJ_4PT): dl_params.inc
$(OBJ_RSQ): dl_params.inc
$(OBJ_NEU): dl_params.inc
$(OBJ_RIG): dl_params.inc
$(OBJ_EXT): dl_params.inc
$(OBJ_SPME): dl_params.inc
```

Appendix B

Periodic Boundary Conditions in DL_POLY

Introduction

DL_POLY_2 is designed to accommodate a number of different periodic boundary conditions, which are defined by the shape and size of the simulation cell. Briefly, these are as follows (which also indicates the IMCON flag defining the simulation cell type in the CONFIG File - see 4.1.2):

1. None e.g. isolated polymer in space. (IMCON=0).
2. Cubic periodic boundaries.(IMCON=1).
3. Orthorhombic periodic boundaries.(IMCON=2).
4. Parallelepiped periodic boundaries.(IMCON=3).
5. Truncated octahedral periodic boundaries. (IMCON=4).
6. Rhombic dodecahedral periodic boundaries. (IMCON=5).
7. Slab (X,Y periodic, Z nonperiodic). (IMCON=6).
8. Hexagonal prism periodic boundaries. (IMCON=7).

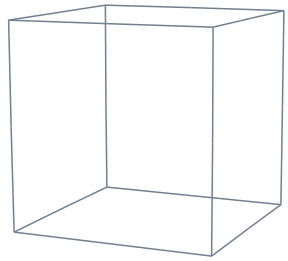
We shall now look at each of these in more detail. Note that in all cases the cell vectors and the positions of the atoms in the cell are to be specified in Angstroms (Å).

No periodic boundary (IMCON=0)

Simulations requiring no periodic boundaries are best suited to *in vacuuo* simulations, such as the conformational study of an isolated polymer molecule. This boundary condition is not recommended for studies in a solvent, since evaporation is likely to be a problem.

Note this boundary condition cannot be used with the Ewald summation method.

Cubic periodic boundaries (IMCON=1)



The cubic MD cell.

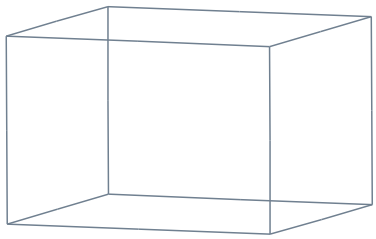
The cubic MD cell is perhaps the most commonly used in simulation and has the advantage of great simplicity. In DL_POLY_2 the cell is defined with the principle axes passing through the centres of the faces. Thus for a cube with sidelength D, the cell vectors appearing in the CONFIG file should be: (D,0,0); (0,D,0); (0,0,D). Note the origin of the atomic coordinates is the centre of the cell.

The cubic boundary condition can be used with the Ewald summation method.

Orthorhombic periodic boundaries (IMCON=2)

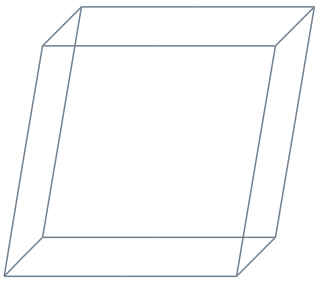
The orthorhombic cell is also a common periodic boundary, which closely resembles the cubic cell in use. In DL_POLY_2 the cell is defined with principle axes passing through the centres of the faces. For an orthorhombic cell with sidelengths D (in X-direction), E (in Y-direction) and F (in Z-direction), the cell vectors appearing in the CONFIG file should be: (D,0,0); (0,E,0); (0,0,F). Note the origin of the atomic coordinates is the centre of the cell.

The orthorhombic boundary condition can be used with the Ewald summation method.



The orthorhomic MD cell.

Parallelepiped periodic boundaries (IMCON=3)

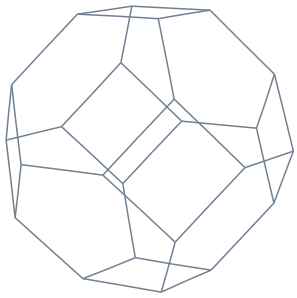


The parallelepiped MD cell.

The parallelepiped (e.g. monoclinic or triclinic) cell is generally used in simulations of crystalline materials, where its shape and dimension is commensurate with the unit cell of the crystal. Thus for a unit cell specified by three principal vectors $\underline{a}$, $\underline{b}$, $\underline{c}$, the MD cell is defined in the DL_POLY_2 CONFIG file by the vectors (La_1,La_2,La_3), (Mb_1,Mb_2,Mb_3), (Nc_1,Mc_2,Nc_3), in which L,M,N are integers, reflecting the multiplication of the unit cell in each principal direction. Note that the atomic coordinate origin is the centre of the MD cell.

The parallelepiped boundary condition can be used with the Ewald summation method.

Truncated octahedral boundaries (IMCON=4)



The truncated octahedral MD cell.

This is one of the more unusual MD cells available in DL_POLY, but it has the advantage of being more nearly spherical than most other MD cells. This means it can accommodate a larger spherical cutoff for a given number of atoms, which leads to greater efficiency. This can be very useful when simulating (for example) a large molecule in solution, where fewer solvent molecules are required for a given simulation cell width.

The principal axes of the truncated octahedron (see figure) pass through the centres of the square faces, and the width of the cell, measured from square face to square face along a principal axis defines the width D of the cell. From this, the cell vectors required in the DL_POLY_2 CONFIG file are simply: (D,0,0), (0,D,0), (0,0,D). These are also the cell vectors defining the enscribing cube, which posseses twice the volume of the truncated octahedral cell. Once again, the atomic positions are defined with respect to the cell centre.

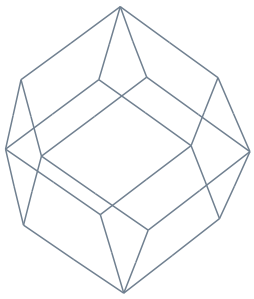
The truncated octahedron can be used with the Ewald summation method.

Rhombic dodecahedral boundaries (IMCON=5)

This is another unusual MD cell (see figure), but which possesses similar advantages to the truncated octahedron, but with a slightly greater efficiency in its use of the cell volume (the ratio is about 74% to 68%).

The principal axis in the X-direction of the rhombic dodecahedron passes through the centre of the cell and the centre of a rhombic face. The Y-axis does likewise, but is set at 90 degrees to the X-axis. The Z-axis completes the orthonormal set and passes through a vertex where four faces meet. If the width D of the cell is defined as the perpendicular distance between two opposite faces, the cell vectors required for the DL_POLY_2 CONFIG file are: (D,0,0), (0,D,0), (0,0,$\sqrt{2}$D).These also define the enscribing orthorhombic cell, which has twice the MD cell volume. In DL_POLY_2 the centre of the cell is also the origin of the atomic coordinates.

The rhombic dodecahedron can be used with the Ewald summation method.



The rhombic dodecahedral MD cell.

Slab boundary conditions (IMCON=6)

Slab boundaries are periodic in the X- and Y-directions, but not in the Z-direction. They are particularly useful for simulating surfaces. The periodic cell in the XY plane can be any parallelogram. The origin of the X,Y atomic coordinates lies on an axis perpendicular to the centre of the parallelogram. The origin of the Z coordinate is where the user specifies it, but at or near the surface is recommended.

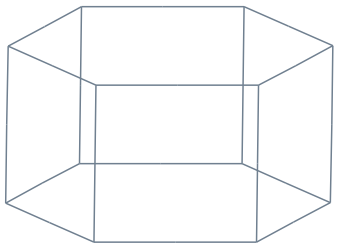
If the XY parallelogram is defined by vectors $\underline{A}$ and $\underline{B}$, the vectors required in the CONFIG file are: (A_1,A_2,0), (B_1,B_2,0), (0,0,D), where D is any real number (including zero). If D is nonzero, it will be used by DL_POLY to help determine a 'working volume' for the system. This is needed to help calculate RDFs etc. (The working value of D is in fact taken as one of: 3×cutoff; or 2×max abs(Z coordinate)+cutoff; or the user specified D, whichever is the larger.)

Note that the Ewald sum cannot be used with this boundary condition.The surface in a system with charges can be modelled with DL_POLY_2 however, if periodicity is allowed in the Z-direction. In this case 'slabs' of ions well-separated by vacuum zones in the Z-direction can be handled with IMCON=2 or 3.

Hexagonal prism boundaries (IMCON=7)

In this case the Z-axis lies along a line joining the centres of the hexagonal faces. The Y-axis is perpendicular to this and passes through the centre of one of the faces. The X-axis completes the orthonormal set and passes through the centre of an edge that is parallel to the Z-axis. (Note: It is important to get this convention right!) The origin of the atomic coordinates is the centre of the cell. If the length of one of the hexagon edges is D, the cell vectors required in the CONFIG file are: (3D,0,0), (0,$\sqrt{3}$D,0), (0,0,H), where H is the prism height (the distance between hexagonal faces). The orthorhombic cell also defined by these vectors enscribes the hexagonal prism and possesses twice the volume, but the height and the centre are the same.

The Ewald summation method may be used with this periodic boundary condition.



The hexagonal MD cell.

This MD cell is particularly suitable for simulating strands or fibres (i.e. systems with a pronounced anisotropy in the Z-direction), such as DNA strands in solution, or stretched polymer chains.

Appendix C

DL_POLY Error Messages and User Action

Introduction

In this appendix we document the error messages encoded in DL_POLY_2 and the recommended user action. The user response to these messages is different according to which version of the code is being run. Versions preceding DL_POLY_2 version 2.11 are significantly different from those appearing after. This is primariliy because version 2.11 intriduced FORTRAN 90 dynamic array allocation, which greatly simplifies the use of the code, but requires a different form of user intervention when array boundaries are violated. The correct response is described as the **standard user response** in the approriate sections below, to which the user should refer before acting on the error encountered.

The reader should also be aware that some of the error messages listed below may be either disabled in, or absent from, the installed version of DL_POLY_2 . Disabled messages generally apply to older releases of the code, while missing messages apply to newer versions of the code and will not usually apply to previous releases. They are all included for completeness. Note that the wording of some of the messages may also have changed over time, usually to provide more specific information. The most recent wording appears below.

DL_POLY_2 Versions 2.10 and Earlier

Many of the DL_POLY_2 error messages refer to array bound checks and the user is advised to consider what other arrays may need to be altered when making the appropriate change. (If you are not familiar with DL_POLY_2 , the error messages will advise you as each array bound is violated, but you will not be told of all errors in one pass.) Users are warned that reckless increases in the array dimensions are likely to result in the code being too large for any given memory. A way to avoid many of these difficulties is to make use of the utility program PARSET (see 6.1.1), which can greatly reduce the work required.

The **standard user response** when an array dimension error occurs is to locate the relevant parameter in the DL_POLY_2 DL_PARAMS.INC file and increase the default number.

It should be remembered that any change in a parameter specified in DL_PARAMS.INC requires the *whole program* to be recompiled. However the standard makefile provided in the *build* directory does this automatically.

DL_POLY_2 Versions 2.11 and Later

Version 2.11 of DL_POLY_2 differs from previous versions in that it incorporates the functionality of the utility code PARSET within the code itself and uses FORTRAN 90 dynamic array allocation to set the array sizes at run time. This is a considerable advance on previous practice and means that a single executable may be compiled to over all the likely uses of the code. It is not foolproof however. Sometimes an estimate of the required array sizes is difficult to obtain and the calculated value may be too small. For this reason DL_POLY_2 retains all the old array dimension checks and will terminate as before when an array bound error occurs.

When a dimension error occurs, the **standard user response** is to edit the DL_POLY_2 subroutine PARSET.F. Locate where the variable defining the array dimension is fixed and increase accordingly. To do this you should make use of the dimension information that DL_POLY_2 prints in the OUTPUT file prior to termination. If no information is supplied, simply doubling the size of the variable will usually do the trick. If the variable concerned is defined in one of the support subroutines CFGSCAN.F, FLDSCAN.F, CONSCAN.F you will need to insert a new line in PARSET.F to redefine it - after the relevant subroutine has been called! Finally the code must be recompiled, but in this case it will be necessary only to recompile PARSET.F and not the whole code.

The DL_POLY_2 Error Messages

Message 1: error - PVM_NODES unset

The code was C-preprocessed with the flag -DPVM set but the number of PVM nodes was not stated.

Action:
Delete the module INITCOMMS.o from the *source* directory and re-make the executable,this time including the directive PVM_NODES=n (where n is the number of nodes you require) with the *make* command.

Message 2: error - machine not a hypercube

The number of nodes on the parallel machine is not a power of 2.

Action:
Specify an appropriate number of processors for job execution. If you are using PVM see *Action:* for error message 1.

Message 3: error - unknown directive found in CONTROL file

This error most likely arises when a directive is misspelt.

Action:
Locate incorrect directive in CONTROL file and replace.

Message 4: error - unknown directive found in FIELD file

This error most likely arises when a directive is misspelt or is encountered in an incorrect location in the FIELD file, which can happen if too few or too many data records are included.

Action:
Locate the erroneous directive in the FIELD file and correct error.

Message 5: error - unknown energy unit requested

The DL_POLY_2 FIELD file permits a choice of units for input of energy parameters. These may be: electron volts (**ev**); kilocalories (**kcal**); kilojoules (**kj**); or the DL_POLY_2 internal units (10 J mol^{-1}) (**internal**). There is no default value. Failure to specify any of these correctly, or reference to other energy units, will result in this error message. See documentation of the FIELD file.

Action:
Correct energy keyword on **units** directive in FIELD file and resubmit.

Message 6: error - energy unit not specified

A **units** directive is mandatory in the FIELD file. This error indicates that DL_POLY_2 has failed to find the required record.

Action:
Add **units** directive to FIELD file and resubmit.

Message 7: error - energy unit respecified

DL_POLY_2 expects only one **units** directive in the FIELD file. This error results if it encounters another - implying an ambiguity in units.

Action:
Locate extra **units** directive in FIELD file and remove.

Message 8: error - time step not specified

DL_POLY_2 requires a **timestep** directive in the CONTROL file. This error results if none is encountered.

Action:
Insert**timestep** directive in CONTROL file with an appropriate numerical value.

Message 10: error - too many molecule types specified

DL_POLY_2 has a set limit on the number of kinds of molecules it will handle in any simulation (this is not the same as the number of molecules). If this permitted maximum is exceeded, the program terminates. The error arises when the **molecules** directive in the FIELD file specifes too large a number.

Action:
Standard user response. Fix parameter `mxtmls`.

Message 11: error - duplicate molecule directive in FIELD file

The number of different types of molecules in a simulation should only be specified once. If DL_POLY_2 encounters more than one **molecules** directive, it will terminate execution.

Action:
Locate the extra **molecule** directive in the FIELD file and remove.

Message 12: error - unknown molecule directive in FIELD file

Once DL_POLY_2 encounters the **molecules** directive in the FIELD file, it assumes the following records will supply data describing the intramolecular force field. It does not then expect to encounter directives not related to these data. This error message results if it encounters a unrelated directive. The most probable cause is incomplete specification of the data (e.g. when the **finish** directive has been omitted.)

Action:
Check the molecular data entries in the FIELD file and correct.

Message 13: error - molecule species not specified

This error arises when DL_POLY_2 encounters non-bonded force data in the FIELD file, *before* the molecular species have been specified. Under these circumstances it cannot assign the data correctly, and therefore terminates.

Action:
Make sure the molecular data appears before the non-bonded forces data in the FIELD file and resubmit.

Message 14: error - too many unique atom types specified

This error arises when DL_POLY_2 scans the FIELD file and discovers that there are too many different types of atoms in the system (i.e. the number of unique atom types exceeds the `mxsvdw` parameter.

Action:
Standard user response. Fix parameter `mxsvdw`.

Message 15: error - duplicate pair potential specified

In processing the FIELD file, DL_POLY_2 keeps a record of the specified short range pair potentials as they are read in. If it detects that a given pair potential has been specified before, no attempt at a resolution of the ambiguity is made and this error message results. See specification of FIELD file.

Action:
Locate the duplication in the FIELD file and rectify.

Message 16: error - strange exit from FIELD file processing

This should never happen! However one remote possibility is that there are more than 10,000 directives in the FIELD file! It simply means that DL_POLY_2 has ceased processing the FIELD data, but has not reached the end of the file or encountered a **close** directive. Probable cause: corruption of the DL_POLY_2 executable or of the FIELD file. We would be interested to hear of other reasons!

Action:
Recompile the program or recreate the FIELD file. If neither of these works, send the problem to us.

Message 17: error - strange exit from CONTROL file processing

See notes on message 16 above.

Message 18: error - duplicate 3-body potential specified

DL_POLY_2 has encountered a repeat specification of a 3-body potential in the FIELD file.

Action:
Locate the duplicate entry, remove and resubmit job.

Message 19: error - duplicate 4-body potential specified

A 4-body potential has been duplicated in the FIELD file.

Action:
Locate the duplicated 4-body potential and remove. Resubmit job.

Message 20: error - too many molecule sites specified

DL_POLY_2 has a fixed limit on the number of unique molecular sites in any given simulation. If this limit is exceeded, the program terminates.

Action:
Standard user response. Fix parameter `mxsite`.

Message 22: error - unsuitable radial increment in TABLE file

This arises when the tabulated potentials presented in the TABLE file have an increment that is greater than that used to define the other potentials in the simulation. Ideally the increment should be $r_{cut}/(mxgrid-4)$, where r_{cut} is the potential cutoff for the short range potentials and `mxgrid` is the parameter defining the length of the interpolation arrays. An increment less than this is permissible however.

Action:
The tables must be recalculated with an appropriate increment.

Message 23: error - incompatible FIELD and TABLE file potentials

This error arises when the specification of the short range potentials is different in the FIELD and TABLE files. This usually means that the order of specification of the potentials is different. When DL_POLY_2 finds a change in the order of specification, it assumes that the user has forgotten to enter one.

Action:
Check the FIELD and TABLE files. Make sure that you correctly specify the pair potentials in the FIELD file, indicating which ones are to be presented in the TABLE file. Then check the TABLE file to make sure all the tabulated potentials are present in the order the FIELD file indicates.

Message 24: error - end of file encountered in TABLE file

This means the TABLE file is incomplete in some way: either by having too few potentials included, or the number of data points is incorrect.

Action:
Examine the TABLE file contents and regenerate it if it appears to be incomplete. If it look intact, check that the number of data points specified is what DL_POLY_2 is expecting.

Message 25: error - wrong atom type found in CONFIG file

On reading the input file CONFIG, DL_POLY_2 performs a check to ensure that the atoms specified in the configuration provided are compatible with the corresponding FIELD file. This message results if they are not.

Action:
The possibility exists that one or both of the CONFIG or FIELD files has incorrectly specified the atoms in the system. The user must locate the ambiguity, using the data printed in the OUTPUT file as a guide, and make the appropriate alteration.

Message 30: error - too many chemical bonds specified

DL_POLY_2 sets a limit on the number of chemical bond potentials that can be specified in the FIELD file. Termination results if this number is exceeded. See FIELD file documentation. Do not confuse this error with that described by message 31 (below).

Action:
Standard user response. Fix parameter `mxtbnd`.

Message 31: error - too many chemical bonds in system

DL_POLY_2 sets a limit on the number of chemical bond potentials in the simulated system as a whole. (This number is a combination of the number of molecules and the number of bonds per molecule, divided by the number of processing nodes.) Termination results if this number is exceeded. Do not confuse this error with that described by message 30 (above).

Action:
Standard user response. Fix the parameter `mxbond`.

Message 32: error - integer array memory allocation failure

DL_POLY_2 has failed to allocate sufficient memory to accommodate one or more of the integer arrays in the code.

Action:
This may simply mean that your simulation is too large for the machine you are running on. Consider this before wasting time trying a fix. Try using more processing nodes if they are available. If this is not an option investigate the possibility of increasing the heap size for your application. Talk to your systems support people for advice on how to do this.

Message 33: error - real array memory allocation failure

DL_POLY_2 has failed to allocate sufficient memory to accommodate one or more of the real arrays in the code.

Action:
This may simply mean that your simulation is too large for the machine you are running on. Consider this before wasting time trying a fix. Try using more processing nodes if they are available. If this is not an option investigate the possibility of increasing the heap size for your application. Talk to your systems support people for advice on how to do this.

Message 34: error - character array memory allocation failure

DL_POLY_2 has failed to allocate sufficient memory to accommodate one or more of the character arrays in the code.

Action:
This may simply mean that your simulation is too large for the machine you are running on. Consider this before wasting time trying a fix. Try using more processing nodes if they are available. If this is not an option investigate the possibility of increasing the heap size for your application. Talk to your systems support people for advice on how to do this.

Message 35: error - logical array memory allocation failure

DL_POLY_2 has failed to allocate sufficient memory to accommodate one or more of the logical arrays in the code.

Action:
This may simply mean that your simulation is too large for the machine you are running on. Consider this before wasting time trying a fix. Try using more processing nodes if they are available. If this is not an option investigate the possibility of increasing the heap size for your application. Talk to your systems support people for advice on how to do this.

Message 40: error - too many bond constraints specified

DL_POLY_2 sets a limit on the number of bond constraints that can be specified in the FIELD file. Termination results if this number is exceeded. See FIELD file documentation. Do not confuse this error with that described by message 41 (below).

Action:
Standard user response. Fix the parameter `mxtcon`.

Message 41: error - too many bond constraints in system

DL_POLY_2 sets a limit on the number of bond constraints in the simulated system as a whole. (This number is a combination of the number of molecules and the number of per molecule, divided by the number of processing nodes.) Termination results if this number is exceeded. Do not confuse this error with that described by message 40 (above).

Action:
Standard user response. Fix the parameter `mxcons`.

Message 42: error - transfer buffer too small in merge1

The buffer used to transfer data between nodes in the MERGE1 subroutines has been dimensioned too small.

Action:
Standard user response. Fix the parameter `mxbuff`.

Message 45: error - too many atoms in CONFIG file

DL_POLY_2 limits the number of atoms in the system to be simulated and checks for the violation of this condition when it reads the CONFIG file. Termination will result if the condition is violated.
Action:
Standard user response. Fix the parameter `mxatms`. Consider the possibility that the wrong CONFIG file is being used (e.g similar system, but larger size.)

Message 46: ewlbuf array too small in ewald1

The `ewlbuf` array used to store structure factor data in subroutine EWALD1 has been dimensioned too small.

Action:
Standard user response. Fix the parameter `mxebuf`.

Message 47: error - transfer buffer too small in merge

The buffer used to transfer data between nodes in the MERGE subroutines has been dimensioned too small.

Action:
Standard user response. Fix the parameter `mxbuff`.

Message 48: error - transfer buffer too small in fortab

The buffer used to transfer data between nodes in the FORTAB subroutines has been dimensioned too small.

Action:
Standard user response. Fix the parameter `mxbuff`.

Message 49: error - frozen core-shell unit specified

The DL_POLY_2 option to freeze the location of an atom (i.e. hold it permanently in one position) is not permitted for core-shell units. This includes freezing the core or the shell independently.

Action:
Remove the frozen atom option from the FIELD file. Consider using a non-polarisable atom instead.

Message 50: error - too many bond angles specified

DL_POLY_2 limits the number of valence angle potentials that can be specified in the FIELD file and checks for the violation of this. Termination will result if the condition is violated. Do not confuse this error with that described by message 51 (below).

Action:
Standard user response. Fix the parameter `mxtang`.

Message 51: error - too many bond angles in system

DL_POLY_2 limits the number of valence angle potentials in the system to be simulated (actually, the number to be processed by each node) and checks for the violation of this. Termination will result if the condition is violated. Do not confuse this error with that described by message 50 (above).

Action:
Standard user response. Fix the parameter `mxangl`. Consider the possibility that the wrong CONFIG file is being used (e.g similar system, but larger size.)

Message 52: error - end of FIELD file encountered

This message results when DL_POLY_2 reaches the end of the FIELD file, without having read all the data it expects. Probable causes: missing data or incorrect specification of integers on the various directives.

Action:
Check FIELD file for missing or incorrect data and correct.

Message 53: error - end of CONTROL file encountered

This message results when DL_POLY_2 reaches the end of the CONTROL file, without having read all the data it expects. Probable cause: missing **finish** directive.

Action:
Check CONTROL file and correct.

Message 55: error - end of CONFIG file encountered

This error arises when DL_POLY_2 attempts to read more data from the CONFIG file than is actually present. The probable cause is an incorrect or absent CONFIG file, but it may be due to the FIELD file being incompatible in some way with the CONFIG file.

Action:
Check contents of CONFIG file. If you are convinced it is correct, check the FIELD file for inconsistencies.

Message 57: error - too many core-shell units specified

DL_POLY_2 has a restriction of the number of types of core-shell unit in the FIELD file and will terminate if too many are present. Do not confuse this error with that described by message 59 (below).

Action:
Standard user response. Fix the parameter `mxtshl`.

Message 59: error - too many core-shell units in system

DL_POLY_2 limits the number of core-shell units in the simulated system. Termination results if too many are encountered. Do not confuse this error with that described by message 57 (above).

Action:
Standard user response. Fix the parameter `mxshl`.

Message 60: error - too many dihedral angles specified

DL_POLY_2 will accept only a limited number of dihedral angles in the FIELD file and will terminate if too many are present. Do not confuse this error with that described by message 61 (below).

Action:
Standard user response. Fix the parameter `mxtdih`.

Message 61: error - too many dihedral angles in system

The number of dihedral angles in the whole simulated system is limited by DL_POLY_2 . Termination results if too many are encountered. Do not confuse this error with that described by message 60 (above).

Action:
Standard user response. Fix the parameter `mxdihd`.

Message 62: error - too many tethered atoms specified

DL_POLY_2 will accept only a limited number of tethered atoms in the FIELD file and will terminate if too many are present. Do not confuse this error with that described by message 63 (below).

Action:
Standard user response. Fix the parameter `mxteth`.

Message 63: error - too many tethered atoms in system

The number of tethered atoms in the simulated system is limited by DL_POLY_2 . Termination results if too many are encountered. Do not confuse this error with that described by message 62 (above).

Action:
Standard user response. Fix the parameter `msteth`.

Message 65: error - too many excluded pairs specified

This error can arise when DL_POLY_2 is identifying the atom pairs that cannot have a pair potential between them, by virtue of being chemically bonded for example (see subroutine EXCLUDE). Some of the working arrays used in this operation may be exceeded, resulting in termination of the program.

Action:
Standard user response. Fix the parameter `mxexcl`.

Message 67: error - incorrect boundary condition in thbfrc

Three body forces in DL_POLY_2 are only permissible with cubic , orthorhombic and parallelepiped periodic boundaries. Use of other boundary conditions results in this error.

Action:
If nonperiodic boundaries are required, the only option is to use a very large simulation cell, with the required system at the centre surrounded by a vacuum. This is not very efficient however and use of a realistic periodic system is the best option.

Message 69: error - too many link cells required in thbfrc

The calculation of three body forces in DL_POLY_2 is handled by the link cell algorithm. This error arises if the required number of link cells exceeds the permitted array dimension in the code.

Action:
Standard user response. Fix the parameter `mxcell`.

Message 70: error - constraint bond quench failure

When a simulation with bond constraints is started, DL_POLY_2 attempts to extract the kinetic energy of the constrained atom-atom bonds arising from the assignment of initial random velocities. If this procedure fails, the program will terminate. The likely cause is a badly generated initial configuration.

Action:
Some help may be gained from increasing the cycle limit, by following the standard user response to increase the control parameter `mxshak`. You may also consider reducing the tolerance of the SHAKE iteration, the directive **shake** in the CONTROL file. However it is probably better to take a good look at the starting conditions!

Message 71: error - too many metal potentials specified

The number of metal potentials that can be specfied in the FIELD file is limited. This error results if too many are used.

Action:
Standard user response. Fix the parameter `mxvdw`. Note that this parameter must be *double* the number of required metal potentials. Recompile the program.

Message 73: error - too many inversion potentials specified

The number of inversion potentials specified in the FIELD file exceeds the permitted maximum.

Action:
Standard user response. Fix the parameter `mxtinv`.

Message 75: error - too many atoms in specified system

DL_POLY_2 places a limit on the number of atoms that can be simulated. Termination results if too many are specified.

Action:
Standard user response. Fix the parameter `mxatms`.

Message 77: error - too many inversion potentials in system

The simulation contains too many inversion potentials overall, causing termination of run.

Action:
Standard user response. Fix the parameter `mxinv`.

Message 79: error - incorrect boundary condition in fbpfrc

The 4-body force routine assumes a cubic or parallelepiped periodic boundary condition is in operation. The job will terminate if this is not adhered to.

Action:
You must reconfigure your simulation to an appropriate boundary condition.

Message 80: error - too many pair potentials specified

DL_POLY_2 places a limit on the number of pair potentials that can be specified in the FIELD file. Exceeding this number results in termination of the program execution.

Action:
Standard user response. Fix the parameters `mxsvdw`. and `mxvdw`.

Message 81: error - unidentified atom in pair potential list

DL_POLY_2 checks all the pair potentials specified in the FIELD file and terminates the program if it can't identify any one of them from the atom types specified earlier in the file.

Action:
Correct the erroneous entry in the FIELD file and resubmit.

Message 82: error - calculated pair potential index too large

In checking the pair potentials specified in the FIELD file DL_POLY_2 calculates a unique integer index that henceforth identifies the potential within the program. If this index becomes too large, termination of the program results.

Action:
Standard user response. Fix the parameters `mxsvdw` and `mxvdw`.

Message 83: error - too many three body potentials specified

DL_POLY_2 has a limit on the number of three body potentials that can be defined in the FIELD file. This error results if too many are included.

Action:
Standard user response. Fix the parameter `mxtbp`.

Message 84: error - unidentified atom in 3-body potential list

DL_POLY_2 checks all the 3-body potentials specified in the FIELD file and terminates the program if it can't identify any one of them from the atom types specified earlier in the file.

Action:
Correct the erroneous entry in the FIELD file and resubmit.

Message 85: error - required velocities not in CONFIG file

If the user attempts to start up a DL_POLY_2 simulation with the **restart** or **restart scale** directives (see description of CONTROL file,) the program will expect the CONFIG file to contain atomic velocities as well as positions. Termination results if these are not present.

Action:
Either replace the CONFIG file with one containing the velocities, or if not available, remove the **restart** directive altogether and let DL_POLY_2 create the velocities for itself.

Message 86: error - calculated 3-body potential index too large

DL_POLY_2 has a permitted maximum for the calculated index for any three body potential in the system (i.e. as defined in the FIELD file). If there are m distinct types of atom in the system, the index can possibly range from 1 to $(m^2 * (m-1))/2$. If the internally calculated index exceeds this number, this error report results.

Action:
Standard user response. Fix the parameter `mxtbp`.

Message 87: error - too many link cells required in fbpfrc

The FBPFRC subroutine uses link cells to compute the four body forces. This message indicates that the link cell arrays have insufficient size to work properly.

Action:
Standard user response. Fix the parameter `mxcell`.

Message 89: error - too many four body potentials specified

Too many four body potential have been defined in the FIELD file. Certain arrays must be increased in size to accommodate the data.

Action:
Standard user response. Fix the parameter `mxfbp`.

Message 90: error - system total electric charge nonzero

In DL_POLY_2 a check on the total system charge will result in an error if the net charge of the system is nonzero. (Note: In DL_POLY_2 this message has been disabled. The program merely prints a warning stating that the system is not electrically neutral but it does not

terminate the program - watch out for this.)

Action:
Check the specified atomic charges and their populations. Make sure they add up to zero. If the system is required to have a net zero charge, you can enable the call to this error message in subroutine SYSDEF.

Message 91: error - unidentified atom in 4-body potential list

The specification of a four-body potential in the FIELD file has referenced an atom type that is unknown.

Action:
Locate the errant atom type in the four body potential definition in the FIELD file and correct. Make sure this atom type is specified by an `atoms` directive earlier in the file.

Message 93: error - cannot use shell model with rigid molecules

The dynamical shell model implemented in DL_POLY_2 is not designed to work with rigid molecules. This error results if these two options are simultaneously selected.

Action:
In some circumstances you may consider overriding this error message and continuing with your simulation. For example if your simulation does not require the polarisability to be a feature of the rigid species, but is confined to free atoms or flexible molecules in the same system. The appropriate error trap is found in subroutine SYSDEF.

Message 95: error - potential cutoff exceeds half cell width

In order for the minimum image convention to work correctly within DL_POLY_2 , it is necessary to ensure that the cutoff applied to the pair potentials does not exceed half the perpendicular width of the simulation cell. (The perpendicular width is the shortest distance between opposing cell faces.) Termination results if this is detected. In NVE simulations this can only happen at the start of a simulation, but in NPT, it may occur at any time.

Action:
Supply a cutoff that is less than half the cell width. If running constant pressure calculations, use a cutoff that will accommodate the fluctuations in the simulation cell. Study the fluctuations in the OUTPUT file to help you with this.

Message 97: error - cannot use shell model with neutral groups

The dynamical shell model was not designed to work with neutral groups. This error results if an attempt is made to combine both.

Action:
There is no general remedy for this error if you wish to combine both these capabilities. However if your simulation does not require the polarisability to be a feature of rigid species (comprising the charged groups), but is confined to free atoms or flexible molecules in the same system, you may consider overriding this error message and continuing with your simulation. The appropriate error trap is found in subroutine SYSDEF.

Message 99: error - cannot use shell model with constraints

The dynamical shell model was not designed to work in conjunction with constraint bonds. This error results if both are used in the same simulation.

Action: There is no general remedy if you wish to combine both these capabilities. However if your simulation does not require the polarisability to be a feature of the constrained species, but is confined to free atoms or flexible molecules, you may consider overriding this error message and continuing with your simulation. The appropriate error trap is in subroutine SYSDEF.

Message 100: error - forces working arrays too small

There are a number of arrays in DL_POLY_2 that function as workspace for the forces calculations. Their dimension is equal to the number of atoms in the simulation cell divided by the number of nodes. If these arrays are likely to be exceeded, DL_POLY_2 will terminate execution.

Action:
Standard user response. Fix the parameter `msatms`.

Message 101: error - calculated 4-body potential index too large

DL_POLY_2 has a permitted maximum for the calculated index for any four body potential in the system (i.e. as defined in the FIELD file). If there are m distinct types of atom in the system, the index can possibly range from 1 to $(m^2 * (m + 1) * (m + 2))/6$. If the internally calculated index exceeds this number, this error report results.

Action:
Standard user response. Fix the parameter `mxfbp`.

Message 102: error - parameter mxproc exceeded in shake arrays

The RD-SHAKE algorithm distributes data over all nodes of a parallel computer. Certain arrays in RD-SHAKE have a minimum dimension equal to the maximum number of nodes DL_POLY_2 is likely to encounter. If the actual number of nodes exceeds this, the program

terminates.

Action:
Standard user response. Fix the parameter `mxproc`.

Message 103: error - parameter mxlshp exceeded in shake arrays

The RD-SHAKE algorithm requires that information about 'shared' atoms be passed between nodes. If there are too many atoms, the arrays holding the information will be exceeded and DL_POLY_2 will terminate execution.

Action:
Standard user response. Fix the parameter `mxlshp`.

Message 105: error - shake algorithm failed to converge

The RD-SHAKE algorithm for bond constraints is iterative. If the maximum number of permitted iterations is exceeded, the program terminates. Possible causes include: a bad starting configuration; too large a time step used; incorrect force field specification; too high a temperature; inconsistent constraints involving shared atoms etc.

Action:
Corrective action depends on the cause. It is unlikely that simply increasing the iteration number will cure the problem, but you can try: follow the standard user response to increase the control parameter `mxshak`. But the trouble is much more likely to be cured by careful consideration of the physical system being simulated. For example, is the system stressed in some way? Too far from equilibrium?

Message 106: error - neighbour list array too small in parlink

Construction of the Verlet neighbour list in subroutine `parlink` nonbonded (pair) force has exceeded the neighbour list array dimensions.

Action:
Standard user response. Fix the parameter `mxlist`.

Message 107: error - neighbour list array too small in parlinkneu

Construction of the Verlet neighbour list in subroutine `parlinkneu` nonbonded (pair) force has exceeded the neighbour list array dimensions.

Action:
Standard user response. Fix the parameter `mxlist`.

Message 108: error - neighbour list array too small in parneulst

Construction of the Verlet neighbour list in subroutine `parneulst` nonbonded (pair) force has exceeded the neighbour list array dimensions.

Action:
Standard user response. Fix the parameter `mxlist`.

Message 109: error - neighbour list array too small in parlst_nsq

Construction of the Verlet neighbour list in subroutine `parlst_nsq` nonbonded (pair) force has exceeded the neighbour list array dimensions.

Action:
Standard user response. Fix the parameter `mxlist`.

Message 110: error - neighbour list array too small in parlst

Construction of the Verlet neighbour list in subroutine `parlst` nonbonded (pair) force has exceeded the neighbour list array dimensions.

Action:
Standard user response. Fix the parameter `mxlist`.

Message 112: error - vertest array too small

This error results when the dimension of the DL_POLY_2 VERTEST arrays, which are used in checking if the Verlet list needs updating, have been exceeded.

Action:
Standard user response. Fix the parameter `mslst`.

Message 120: error - invalid determinant in matrix inversion

DL_POLY_2 occasionally needs to calculate matrix inverses (usually the inverse of the matrix of cell vectors, which is of size 3×3). For safety's sake a check on the determinant is made, to prevent inadvertent use of a singular matrix.

Action:
Locate the incorrect matrix and fix it - e.g. are cell vectors correct?

Message 130: error - incorrect octahedral boundary condition

When calculating minimum images DL_POLY_2 checks that the periodic boundary of the simulation cell is compatible with the specifed minimum image algorithm. Program termination results if an inconsistency is found. In this case the error refers to the truncated

octahedral minimum image, which is inconsistent with the simulation cell. The most probable cause is the incorrect definition of the simulation cell vectors present in the input file CONFIG, these must equal the vectors of the enscribing cubic cell.

Action:
Check the specified simulation cell vectors and correct accordingly.

Message 135: error - incorrect hexagonal prism boundary condition

When calculating minimum images DL_POLY_2 checks that the periodic boundary of the simulation cell is compatible with the specifed minimum image algorithm. Program termination results if an inconsistency is found. In this case the error refers to the hexagonal prism minimum image, which is inconsistent with the simulation cell. The most probable cause is the incorrect definition of the simulation cell vectors present in the input file CONFIG, these must equal the vectors of the enscribing orthorhombic cell.

Action:
Check the specified simulation cell vectors and correct accordingly.

Message 140: error - incorrect dodecahedral boundary condition

When calculating minimum images DL_POLY_2 checks that the periodic boundary of the simulation cell is compatible with the specifed minimum image algorithm. Program termination results if an inconsistency is found. In this case the error refers to the rhombic dodecahedral minimum image, which is inconsistent with the simulation cell. The most probable cause is the incorrect definition of the simulation cell vectors present in the input file CONFIG, these must equal the vectors of the enscribing tetragonal simulation cell.

Action:
Check the specified simulation cell vectors and correct accordingly.

Message 145: error - no van der waals potentials defined

This error arises when there are no VDW potentials specified in the FIELD file but the user has not specified **no vdw** in the CONTROL file. In other words DL_POLY_2 expects the FIELD file to contain VDW potential specifications.

Action:
Edit the FIELD file to insert the required potentials or specify **no vdw** in the CONTROL file.

Message 150: error - unknown van der waals potential selected

DL_POLY_2 checks when constructing the interpolation tables for the short ranged potentials that the potential function requested is one which is of a form known to the program.

If the requested potential form is unknown, termination of the program results. The most probable cause of this is the incorrect choice of the potential keyword in the FIELD file or one in the wrong columns (input is formatted).

Action:
Read the DL_POLY_2 documentation and find the potential keyword for the potential desired. Insert the correct index in the FIELD file definition and ensure it occurs in the correct columns (17-20). If the correct form is not available, look at the subroutine FORGEN (or its variant) and define the potential for yourself. It is easily done.

Message 151: error - unknown metal potential selected

The metal potentials available in DL_POLY_2 are confined to density dependent forms of the Sutton-Chen type. This error results if the user attempts to specify another.

Action:
Re-specify the potential as Sutton-Chen type if possible. Check the potential keyword appears in columns 17-20 of the FIELD file.

Message 153: error - metals not permitted with multiple timestep

The multiple timestep algorithm cannot be used in conjunction with metal potentials in DL_POLY_2 .

Action:
The simulation must be run without the multiple timestep option.

Message 160: error - unaccounted for atoms in exclude list

This error message means that DL_POLY_2 has been unable to find all the atoms described in the exclusion list within the simulation cell. This should never occur, if it does it means a serious bookkeeping error has occured. The probable cause is corruption of the code somehow.

Action:
If you feel you can tackle it - good luck! Otherwise we recommend you get in touch with the program authors. Keep all relevant data files to help them find the problem.

Message 170: error - too many variables for statistic array

This error means the statistics arrays appearing in subroutine STATIC are too small. This can happen if the number of unique atom types is too large.

Action:
Standard user response. Fix the parameter `mxnstk`. `mxnstk` should be at least (45+*number of unique atom types*).

Message 180: error - Ewald sum requested in non-periodic system

DL_POLY_2 can use either the Ewald method or direct summation to calculate the electrostatic potentials and forces in periodic (or pseudo-periodic) systems. For non-periodic systems only direct summation is possible. If the Ewald summation is requested (with the **ewald sum** or **ewald precision** directives in the CONTROL file) without periodic boundary conditions, termination of the program results.

Action:
Select periodic boundaries by setting the variable `imcon`>0 in the CONFIG file (if possible) or use a different method to evaluate electrostatic interactions e.g. by usinf the **coul** directive in the CONTROL file.

Message 185: error - too many reciprocal space vectors

DL_POLY_2 places hard limit on the number of k vectors to be used in the Ewald sum and terminates if more than this is requested.

Action:
Either consider using fewer k vectors in the Ewald sum (and a larger cutoff in real space) or follow standard user response to reset the parameters `kmaxb, kmaxc`.

Message 186: error - transfer buffer array too small in sysgen

In the subroutine SYSGEN.F DL_POLY_2 requires dimension of the array `buffer` (defined by the parameter `mxbuff`) to be no less than the parameter `mxatms` or the product of parameters `mxnstk*mxstak`. If this is not the case it will be unable to restart the program correctly to continue a run. (Applies to parallel implementations only.)

Action:
Standard user response. Fix the parameter `mxbuff`.

Message 190: error - buffer array too small in splice

DL_POLY_2 uses a workspace array named `buffer` in several routines. Its declared size is a compromise of several rôles and may sometimes be too small (though in the supplied program, this should happen only very rarely). The point of failure is in the SPLICE routine, which is part of the RD-SHAKE algorithm.

Action:
Standard user response. Fix the parameter `mxbuff`.

Message 200: error - rdf buffer array too small in revive

This error indicates that the buffer array used to globally sum the rdf arrays in subroutine REVIVE is too small.

Action:
Standard user response. Fix the parameter `mxbuff`. Alternatively `mxrdf` can be set smaller.

Message 220: error - too many neutral groups in system

DL_POLY_2 has a fixed limit on the number of charged groups in a simulation. This error results if the number is exceeded.

Action:
Standard user response. Fix the parameter `mxneut`.

Message 230: error - neutral groups improperly arranged

In the DL_POLY_2 FIELD file the charged groups must be defined in consecutive order. This error results if this convention is not adhered to.

Action:
The arrangement of the data in the FIELD file must be sorted. All atoms in the same group must be arranged consecutively. Note that reordering the file in this way implies a rearrangement of the CONFIG file also.

Message 250: error - Ewald sum requested with neutral groups

DL_POLY_2 will not permit the use of neutral groups with the Ewald sum. This error results if the two are used together.

Action:
Either remove the **neut** directive from the FIELD file or use a different method to evaluate the electrostatic interactions.

Message 260: error - parameter mxexcl exceeded in excludeneu routine

An error has been detected in the construction of the excluded atoms list for neutral groups. This occurs when the parameter `mxexcl` is exceeded in the EXCLUDENEU routine.

Action:
Standard user response. Fix parameter `mxexcl`.

Message 300: error - incorrect boundary condition in parlink

The use of link cells in DL_POLY_2 implies the use of appropriate boundary conditions. This error results if the user specifies octahedral, dodecahedral or slab boundary conditions.

Action:
The simulation must be run with cubic, orthorhombic or parallelepiped boundary conditions.

Message 301: error - too many rigid body types

The maximum number of rigid body types permitted by DL_POLY_2 has been exceeded.

Action:
Standard user response. Fix the parameter `mxungp`.

Message 302: error - too many sites in rigid body

This error arises when DL_POLY_2 finds that the number of sites in a rigid body exceeds the dimensions of the approriate storage arrays.

Action:
Standard user response. Fix the parameter `mxngp`.

Message 303: error - too many rigid bodies specified

The maximum number of rigid bodies in a simulation has been reached. Do not confuse this with message 304 below.

Action:
Standard user response. Fix the parameter `mxgrp`.

Message 304: error - too many rigid body sites in system

This error occurs when the total number of sites within all rigid bodies exceeds the permitted maximum. Do not confuse this with message 303 above.

Action:
Standard user response. Fix the parameter `mxgatms`.

Message 305: error - box size too small for link cells

The link cells algorithm in DL_POLY_2 cannot work with less than 27 link cells. Depending on the cell size and the chosen cut-off, DL_POLY_2 may decide that this minimum cannot be achieved and terminate.

Action:
If a smaller cut-off is acceptable use it. Otherwise do not use link cells. Consider running a larger system, where link cells will work.

Message 306: error - failed to find principal axis system

This error indicates that the routine QUATBOOK has failed to find the principal axis for a rigid unit.

Action:
This is an unlikely error. The code should correctly handle linear, planar and 3-dimensional rigid units. Check the definition of the rigid unit in the CONFIG file, if sensible report the error to the authors.

Message 310: error - quaternion setup failed

This error indicates that the routine QUATBOOK has failed to reproduce all the atomic positions in rigid units from the centre of mass and quaternion vectors it has calculated.

Action:
Check the contents of the CONFIG file. DL_POLY_2 builds its local body description of a rigid unit type from the *first* occurrence of such a unit in the CONFIG file. The error most likely occurs because subsequent occurrences were not sufficiently similar to this reference structure. If the problem persists increase the value of the variable `tol` in QUATBOOK and recompile. If problems still persist double the value of `dettest` in QUATBOOK and recompile. If you still encounter problems contact the authors.

Message 320: error - site in multiple rigid bodies

DL_POLY_2 has detected that a site is shared by two or more rigid bodies. There is no integration algorithm available in this version of the package to deal with this type of model.

Action:
The only course is to redefine the molecular model (e.g. introducing flexible bonds and angles in suitable places) to allow DL_POLY_2 to proceed.

Message 321: error - quaternion integrator failed

The quaternion algorithm has failed to converge. If the maximum number of permitted iterations is exceeded, the program terminates. Possible causes include: a bad starting configuration; too large a time step used; incorrect force field specification; too high a temperature; inconsistent constraints involving shared atoms etc.

Action:
Corrective action depends on the cause. Try reducing the timestep or running a zero kelvin

structure optimization for a hundred timesteps or so. It is unlikely that simply increasing the iteration number will cure the problem, but you can try: follow the standard user response to increase the parameter `mxquat`. But the trouble is much more likely to be cured by careful consideration of the physical system being simulated. For example, is the system stressed in some way? Too far from equilibrium?

Message 330: error - mxewld parameter incorrect

DL_POLY_2 has two strategies for parallelization of the reciprocal space part of the Ewald sum. If EWALD1 is used the parameter `mxewld` should equal the parameter `msatms`. If EWALD1A is used this parameter should equal `mxatms`.

Action:
Standard user response. Set the parameter `mxewld` to the value appropriate for the version of EWALD1 you are using. Recompile the program.

Message 340: error - invalid integration option requested

DL_POLY_2 has detected an incompatibility in the simulation instructions, namely that the requested integration algorithm is not compatible with the physical model. It *may* be possible to override this error trap, but it is up to the user to establish if this is sensible.
Action:
This is a non recoverable error, unless the user chooses to override the restriction.

Message 350: error - too few degrees of freedom

This error can arise if a small system is being simulated and the number of constraints applied is too large.

Action:
Simulate a larger system or reduce the number of constraints.

Message 360: error - frozen atom found in rigid body

DL_POLY_2 does not permit a site in a rigid body to be frozen i.e. fixed in one location in space.

Action:
Remove the 'freeze' condition from the site concerned. Consider using a very high site mass to achieve a similar effect.

Message 380: error - simulation temperature not specified

DL_POLY_2 has failed to find a **temp** directive in the CONTROL file.

Action:
Place a **temp** directive in the CONTROL file, with the required temperature specified.

Message 381: error - simulation timestep not specified

DL_POLY_2 has failed to find a **timestep** directive in the CONTROL file.

Action:
Place a **timestep** directive in the CONTROL file, with the required timestep specified.

Message 382: error - simulation cutoff not specified

DL_POLY_2 has failed to find a **cutoff** directive in the CONTROL file.

Action:
Place a **cutoff** directive in the CONTROL file, with the required forces cutoff specified.

Message 383: error - simulation forces option not specified

DL_POLY_2 has failed to find any directive specifying the electrostatic interactions options in the CONTROL file.

Action:
Ensure the CONTROL file contains at least one directive specifying the electrostatic potentials (e.g. **ewald**, **coul**, **no electrostatics** etc.)

Message 384: error - verlet strip width not specified

DL_POLY_2 has failed to find the **delr** directive in the CONTROL file.

Action:
Insert a **delr** directive in the CONTROL file, specifying the width of the verlet strip augmenting the forces cutoff.

Message 385: error - primary cutoff not specified

DL_POLY_2 has failed to find the **prim** directive in the CONTROL file. Necessary only if multiple timestep option required.

Action:
Insert a **prim** directive in the CONTROL file, specifying the primary cutoff radius in the multiple timestep algorithm.

Message 386: error - primary cutoff larger than rcut

The primary cutoff specified by the **prim** directive in the CONTROL file exceeds the value specified for the forces cutoff (directive **cut**). Applies only if the multiple timestep option is required.

Action:
Locate the **prim** directive in the CONTROL file, and alter the chosen cutoff. Alternatively, increase the real space cutoff specified with the **cut** directive. Take care to avoid error number 398.

Message 387: error - system pressure not specified

The target system pressure has not been specified in the CONTROL file. Applies to NPT simulations only.

Action:
Insert a **press** directive in the CONTROL file specifying the required system pressure.

Message 388: error - npt incompatible with multiple timestep

The use of NPT (constant pressure) and temperature is not compatible with the multiple timestep option.

Action:
Simulation must be run at fixed volume in this case. But note it may be possible to use NPT without the multiple timestep, in ourder to estimate the required system volume, then switch back to multiple timestep and NVT dynamics at the required volume.

Message 390: error - npt ensemble requested in non-periodic system

A non-periodic system has no defined volume, hence the NPT algorithm cannot be applied.

Action:
Either simulate the system with a periodic boundary, or use another ensemble.

Message 392: error - too many link cells requested

The number of link cells required for a given simulation exceeds the number allowed for by the DL_POLY_2 arrays.

Action:
Standard user response. Fix the parameter `mxcell`.

Message 394: error - minimum image arrays exceeded

The work arrays used in IMAGES have been exceeded.
Action: Standard user response. Fix the parameter `mxxdf`.

Message 396: error - interpolation array exceeded

DL_POLY_2 has sought to read past the end of an interpolation array. This should never happen!

Action:
Contact the authors.

Message 398: error - cutoff too small for rprim and delr

This error can arise when the multiple timestep option is used. It is essential that the primary cutoff (`rprim`) is less than the real space cutoff (`rcut`) by at least the Verlet shell width `delr` (preferably much larger!). DL_POLY_2 terminates the run if this condition is not satisfied.

Action:
Adjust `rcut`, `rprim` and `delr` to satisfy the DL_POLY_2 requirement. These are defined with the directives **cut**, **prim** and **delr** respectively.

Message 400: error - rvdw greater than cutoff

DL_POLY_2 requires the real space cutoff (`rcut`) to be larger than, or equal to, the van der Waals cutoff (`rvdw`) and terminates the run if this condition is not satisfied.

Action:
Adjust `rvdw` and `rcut` to satisfy the DL_POLY_2 requirement.

Message 402: error - van der waals cutoff unset

The user has not set a cutoff (`rvdw`) for the van der Waals potentials. The simulation cannot proceed without this being specified.

Action:
Supply a cutoff value for the van der Waals terms in the CONTROL file using the directive **rvdw**, and resubmit job.

Message 410: error - cell not consistent with image convention

The simulation cell vectors appearing in the CONFIG file are not consistent with the specified image convention.

Action:
Locate the variable `imcon` in the CONFIG file and correct to suit the cell vectors.

Message 412: error - mxxdf parameter too small for shake routine

In DL_POLY_2 the parameter `mxxdf` must be greater than or equal to the parameter `mxcons`. If it is not, this error is a possible result.

Action:
Standard user response. Fix the parameter `mxxdf`.

Message 414: error - conflicting ensemble options in CONTROL file

DL_POLY_2 has found more than one **ensemble** directive in the CONTROL file.

Action:
Locate extra **ensemble** directives in CONTROL file and remove.

Message 416: error - conflicting force options in CONTROL file

DL_POLY_2 has found incompatible directives in the CONTROL file specifying the electrostatic interactions options.

Action:
Locate the conflicting directives in the CONTROL file and correct.

Message 418: error - bond vector work arrays too small in bndfrc

The work arrays in BNDFRC have been exceeded.

Action:
Standard user response. Fix the parameter `msbad`.

Message 419: error - bond vector work arrays too small in angfrc

The work arrays in ANGFRC have been exceeded.

Action:
Standard user response. Fix the parameter `msbad`.

Message 420: error - bond vector work arrays too small in tethfrc

The work arrays in TETHFRC have been exceeded.

Action:
Standard user response. Fix the parameter `msbad`.

Message 421: error - bond vector work arrays too small in dihfrc

The work arrays in DIHFRC have been exceeded.

Action:
Standard user response. Fix the parameter `msbad`.

Message 422: error - all-pairs must use multiple timestep

In DL_POLY_2 the 'all pairs' option must be used in conjunction with the multiple timestep.

Action:
Activate the multiple timestep option in the CONTROL file and resubmit.

Message 423: error - bond vector work arrays too small in shlfrc

The dimensions of the interatomic distance vectors have been exceeded in subroutine SHLFRC.

Action:
Standard user response. Fix the parameter `msbad`. Set equal to the value of the parameter `mxshl`.

Message 424: error - electrostatics incorrect for all-pairs

When using the all pairs option in conjunction with electrostatic forces, the electrostatics must be handled with either the standard Coulomb sum, or with the distance dependent dielectric.

Action:
Rerun the simulation with the appropriate electrostatic option.

Message 425: error - transfer buffer array too small in shlmerge

The buffer used to transfer data between nodes in the subroutine SHLMERGE has been dimensioned too small.

Action:
Standard user response. Fix the parameter `mxbuff`.

Message 426: error - neutral groups not permitted with all-pairs

DL_POLY_2 will not permit simulations using both the neutral group and all pairs options together.

Action:
Switch off one of the conflicting options and rerun.

Message 427: error - bond vector work arrays too small in invfrc

The work arrays in subroutine INVFRC have been exceeded.

Action:
Standard user response. Fix the parameter `msbad`.

Message 430: error - integration routine not available

A request for a nonexistent ensemble has been made or a request with conflicting options that DL_POLY_2 cannot deal with (e.g. a Evans thermostat with rigid body equations of motion).

Action:
Examine the CONTROL and FIELD files and remove inappropriate specifications.

Message 432: error - intlist failed to assign constraints

If the required simulation has constraint bonds DL_POLY_2 attempts to apportion the molecules to processors so that, if possible, there are no shared atoms between processors. If this is not possible, one or more molecules may be split between processors. This message indicates that the code has failed to carry out either of these successfully.

Action:
The error may arise from a compiler error. Try recompiling INTLIST without the optimization flag turned on. If the problem persists it should be reported to the authors, (after checking the input data for inconsistencies).

Message 433: error - specify rcut before the Ewald sum precision

When specifying the desired precision for the Ewald sum in the CONTROL file, it is first necessary to specify the real space cutoff `rcut`.

Action:
Place the **cut** directive *before* the **ewald precision** directive in the CONTROL file and rerun.

Message 434: error - illegal entry into STRESS related routine

The calculation of the stress tensor in DL_POLY_2 requires additional code that must be included at compile time through the use of the STRESS keyword. If this is not done, and

DL_POLY_2 is later required to calculate the stress tensor, this error will result.

Action:
The program must be recompiled with the STRESS keyword activated. This will ensure all the relevant code is in place. See section 3.2.1.

Message 436: error - unrecognised ensemble

An unknown ensemble option has been specified in the CONTROL file.

Action:
Locate **ensemble** directive in the CONTROL file and amend appropriately.

Message 438: error - PMF constraints failed to converge

The constraints in the potential of mean force algorithm have not converged in the permitted number of cycles. (The SHAKE algorithm for PMF constraints is iterative.) Possible causes include: a bad starting configuration; too large a time step used; incorrect force field specification; too high a temperature; inconsistent constraints involving shared atoms etc.

Action:
Corrective action depends on the cause. It is unlikely that simply increasing the iteration number will cure the problem, but you can try: follow standard user response to increase the parameter `mxshak`. But the trouble is much more likely to be cured by careful consideration of the physical system being simulated. For example, is the system stressed in some way? Too far from equilibrium?

Message 440: error - undefined angular potential

A form of angular potential has been requested which DL_POLY_2 does not recognise.

Action:
Locate the offending potential in the FIELD file and remove. Replace with one acceptable to DL_POLY_2 if this is possible. Alternatively, you may consider defining the required potential in the code yourself. Amendments to subroutines SYSDEF and ANGFRC will be required.

Message 442: error - undefined three body potential

A form of three body potential has been requested which DL_POLY_2 does not recognise.

Action:
Locate the offending potential in the FIELD file and remove. Replace with one acceptable to DL_POLY_2 if this is reasonable. Alternatively, you may consider defining the required

potential in the code yourself. Amendments to subroutines SYSDEF and THBFRC will be required.

Message 443: error - undefined four body potential

DL_POLY_2 has been requested to process a four-body potential it does not recognise.

Action:
Check the FIELD file and make sure the keyword is correctly defined. Make sure that subroutine FBPFRC contains the code necessary to deal with the requested potential. Add the code required if necessary, by amending subroutines SYSDEF and FBPFRC.

Message 444: error - undefined bond potential

DL_POLY_2 has been requested to process a bond potential it does not recognise.

Action:
Check the FIELD file and make sure the keyword is correctly defined. Make sure that subroutine BNDFRC contains the code necessary to deal with the requested potential. Add the code required if necessary, by amending subroutines SYSDEF and BNDFRC.

Message 446: error - undefined electrostatic key in dihfrc

The subroutine DIHFRC has been requested to process a form of electrostatic potential it does not recognise.

Action:
The error arises because the integer key `keyfrc` has an inappropriate value (which should not happen in the standard version of DL_POLY_2). Check that the FIELD file correctly specifies the potential. Make sure the version of DIHFRC does contain the potential you are specifying. Report the error to the authors if these checks are correct.

Message 448: error - undefined dihedral potential

A form of dihedral potential has been requested which DL_POLY_2 does not recognise.

Action:
Locate the offending potential in the FIELD file and remove. Replace with one acceptable to DL_POLY_2 if this is reasonable. Alternatively, you may consider defining the required potential in the code yourself. Amendments to subroutines SYSDEF and DIHFRC (and its variants) will be required.

Message 449: error - undefined inversion potential

A form of inversion potential has been encountered which DL_POLY_2 does not recognise.

Action:
Locate the offending potential in the FIELD file and remove. Replace with one acceptable to DL_POLY_2 if this is reasonable. Alternatively, you may consider defining the required potential in the code yourself. Amendments to subroutines SYSDEF and INVFRC will be required.

Message 450: error - undefined tethering potential

A form of tethering potential has been requested which DL_POLY_2 does not recognise.

Action:
Locate the offending potential in the FIELD file and remove. Replace with one acceptable to DL_POLY_2 if this is reasonable. Alternatively, you may consider defining the required potential in the code yourself. Amendments to subroutines SYSDEF and TETHFRC will be required.

Message 451: error - three body potential cutoff undefined

The cutoff radius for a three body potential has not been defined in the FIELD file.

Action:
Locate the offending three body force potential in the FIELD file and add the required cutoff. Resubmit the job.

Message 452: error - undefined pair potential

A form of pair potential has been requested which DL_POLY_2 does not recognise.

Action:
Locate the offending potential in the FIELD file and remove. Replace with one acceptable to DL_POLY_2 if this is reasonable. Alternatively, you may consider defining the required potential in the code yourself. Amendments to subroutines SYSDEF and FORGEN will be required.

Message 453: error - four body potential cutoff undefined

The cutoff radius for a four-body potential has not been defined in the FIELD file.

Action:
Locate the offending four body force potential in the FIELD file and add the required cutoff. Resubmit the job.

Message 454: error - undefined external field

A form of external field potential has been requested which DL_POLY_2 does not recognise.

Action:
Locate the offending potential in the FIELD file and remove. Replace with one acceptable to DL_POLY_2 if this is reasonable. Alternatively, you may consider defining the required potential in the code yourself. Amendments to subroutines SYSDEF and EXTNFLD will be required.

Message 456: error - core and shell in same rigid unit

It is not sensible to fix both the core and the shell of a polarisable atom in the same molecular unit. Consequently DL_POLY_2 will abandon the job if this is found to be the case.

Action:
Locate the offending core-shell unit (there may be more than one in your FIELD file) and release the shell (preferably) from the rigid body specification.

Message 458: error - too many PMF constraints - param. mspmf too small

The number of constraints in the potential of mean force is too large. The dimensions of the appropriate arrays in DL_POLY_2 must be increased.

Action:
Standard user response. Fix the parameter `mspmf`.

Message 460: error - too many PMF sites - parameter mxspmf too small

The number of sites defined in the potential of mean force is too large. The dimensions of the appropriate arrays in DL_POLY_2 must be increased.

Action:
Standard user response. Fix the parameter `mxspmf`.

Message 462: error - PMF UNIT record expected

A **pmf unit** directive was expected as the next record in the FIELD file but was not found.

Action:
Locate the **pmf** directive in the FIELD file and examine the following entries. Insert the missing **pmf unit** directive and resubmit.

Message 464: error - thermostat time constant must be > 0.d0

A zero or negative value for the thermostat time constant has been encountered in the CONTROL file.

Action:
Locate the **ensemble** directive in the CONTROL file and assign a positive value to the time constant.

Message 466: error - barostat time constant must be > 0.d0

A zero or negative value for the barostat time constant has been encountered in the CONTROL file.

Action:
Locate the **ensemble** directive in the CONTROL file and assign a positive value to the time constant.

Message 468: error - r0 too large for snm potential with current cutoff

The specified location (r0) of the potential minimum for a shifted n-m potential exceeds the specified potential cutoff. A potential with the desired minimum cannot be created.

Action:
To obtain a potential with the desired minimum it is necessary to increase the van der Waals cutoff. Locate the **rvdw** directive in the CONTROL file and reset to a magnitude greater than r0. Alternatively adjust the value of r0 in the FIELD file. Check that the FIELD file is correctly formatted.

Message 470: error - n<m in definition of n-m potential

The specification of a n-m potential in the FIELD file implies that the exponent m is larger than exponent n. (Not all versions of DL_POLY_2 are affected by this.)

Action:
Locate the n-m potential in the FIELD file and reverse the order of the exponents. Resubmit the job.

Message 474: error - mxxdf too small in parlst subroutine

The parameter `mxxdf` defining working arrays in subroutine PARLST of DL_POLY_2 has been found to be too small.

Action:
Standard user response. Fix the parameter `mxxdf`.

Message 475: error - mxxdf too small in parlst_nsq subroutine

The parameter `mxxdf` defining working arrays in subroutine PARLST_NSQ DL_POLY_2 has been found to be too small.

Action:
Standard user response. Fix the parameter `mxxdf`.

Message 476: error - mxxdf too small in parneulst subroutine

The parameter `mxxdf` defining working arrays in subroutine PARNEULST is too small.

Action:
Standard user response. Fix the parameter `mxxdf`.

Message 477: error - mxxdf too small in prneulst subroutine

The parameter `mxxdf` defining working arrays in subroutine PRNEULST is too small.

Action:
Standard user response. Fix the parameter `mxxdf`.

Message 478: error - mxxdf too small in forcesneu subroutine

The parameter `mxxdf` defining working arrays in subroutine FORCESNEU is too small.

Action:
Standard user response. Fix the parameter `mxxdf`.

Message 479: error - mxxdf too small in multipleneu subroutine

The parameter `mxxdf` defining working arrays in subroutine MULTIPLENEU is too small.

Action:
Standard user response. Fix the parameter `mxxdf`.

Message 484: error - only one potential of mean force permitted

It is not permitted to define more than one potential of mean force in the FIELD file.

Action:
Check that the FIELD file contains only one PMF specification. If more than one is needed, DL_POLY_2 cannot handle it.

Message 490: error - PMF parameter mxpmf too small in passpmf

The bookkeeping arrays have been exceeded in PASSPMF

Action:
Standard user response. Fix the parameter `mxpmf`. Set equal to `mxatms`.

Message 492: error - parameter mxcons < number of PMF constraints

The parameter `mxcons` is too small for the number of PMF constraints in the system.

Action:
Standard user response. Fix the value of `mxcons`.

Message 494: error in csend: pvmfinitsend

The PVM routine PVMFINITSEND has returned an error. It is invoked by the routine CSEND.

Action:
Check your system implementation of PVM.

Message 496: error in csend: pvmfpack

The PVM routine PVMFPACK has returned an error. It is invoked by the routine CSEND.

Action:
Check your system implementation of PVM.

Message 498: error in csend: pvmfsend

The PVM routine PVMFSEND has returned an error. It is invoked by the routine CSEND.

Action:
Check your system implementation of PVM.

Message 500: error in crecv: pvmfrecv

The PVM routine PVMFRECV has returned an error. It is invoked by the routine CRECV.

Action:
Check your system implementation of PVM.

Message 502: error in crecv: pvmfunpack

The PVM routine PVMFUNPACK has returned an error. It is invoked by the routine CRECV.

Action:
Check your system implementation of PVM.

Message 504: error - cutoff too large for TABLE file

The requested cutoff exceeds the information in the TABLE file.

Action:
Reduce the value of the vdw cutoff (`rvdw`) in the CONTROL file or reconstruct the TABLE file.

Message 506: error - work arrays too small for quaternion integration

The working arrays associated with quaternions are too small for the size of system being simulated. They must be redimensioned.

Action:
Standard user response. Fix the parameter `msgrp`.

Message 508: error - rigid bodies not permitted with RESPA algorithm

The RESPA algorithm implemented in DL_POLY_2 is for atomic systems only. Rigid bodies or constraints cannot be treated.

Action:
There is no cure for this. The code simply does not have this capability. Consider writing it for yourself!

Message 510: error - structure optimiser not permitted with RESPA

The RESPA algorithm in DL_POLY_2 has not been implemented to work with the structure optimizer. You have asked for a forbidden operation.

Action:
There is no fix for this. In any case it does not make sense to use the RESPA algorithm for this purpose.

Message 513: error - SPME not available for given boundary conditions

The SPME algorithm in DL_POLY_2 does not work for aperiodic (IMCON=0) or slab (IMCON=6) boundary conditions.
Action:
If the system must have aperiodic or slab boundaries, nothing can be done. In the latter case however, it may be acceptable to represent the same system with slabs replicated in the z direction, thus permitting a periodic simulation.

Message 514: error - SPME routines have not been compiled in

The inclusion of the SPME algorithm in DL_POLY_2 is optional at the compile stage. If the executable does not contain the SPME routines, but the method is requested by the user, this error results.

Action:
DL_POLY_2 must be recompiled with the SPME flags set. Beware that your system has the necessary fast Fourier transform routines to permit this.